

THE ELEMENTS OF PHYSICAL CHEMISTRY

F. W. GODDARD
&
E. J. F. JAMES

[illegible]

K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Cs	Ba	La	Ce	Pr	to	Yb	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl
55	56	57	58	59	to	70	71	72	73	74	75	76	77	78	79	80	81
Fr	Ra	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Mn	Ni	Pb	Bi
87	88	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	104

Period	Group 0	Group 1 A	Group 1 B	Group 2 A	Group 2 B	Group 3 A	Group 3 B	Group 4 A	Group 4 B	Group 5 A	Group 5 B	Group 6 A	Group 6 B	Group 7 A	Group 7 B	Group 8	
1		1 H 1.008															
2 1st short period	2 He 4.003	3 Li 6.94		4 Be 9.013	5 B 10.82			6 C 12.01		7 N 14.008		8 O 16		9 F 19			
3 2nd short period	10 Ne 20.183	11 Na 22.997		12 Mg 24.32	13 Al 26.98			14 Si 28.09		15 P 30.975		16 S 32.066		17 Cl 35.457			
4 1st long period	18 Ar 39.944	19 K 39.1		20 Ca 40.08	21 Sc 44.96			22 Ti 47.90		23 V 50.95		24 Cr 52.01		25 Mn 54.93	26 Fe 55.85	27 Co 58.94	28 Ni 58.69
5 2nd long period	36 Kr 83.8	37 Rb 85.48		38 Sr 87.63	39 Y 88.92			40 Zr 91.22		41 Nb 92.91		42 Mo 95.95		43 Tc —	44 Ru 101.7	45 Rh 102.91	46 Pd 106.7
6 3rd long period	54 Xe 131.3	55 Cs 132.91		56 Ba 137.36	57 La 138.92 58-71 The rare earths *			58 Ce 137.4		59 Pr 140.92		60 Nd 144.27		61 Pm —	62 Sm 150.43	63 Eu 152.0	64 Gd 157.25
7	86 Rn 222	87 Fr —		88 Ra 226.05	89 Ac 227			90 Th 232.04		91 Pa 231		92 U 238.03		93 Np —	94 Pu 244	95 Am 243	96 Cm 247

Typical elements

* The rare earths	58 Ce 140.13	59 Pr 140.92	60 Nd 144.27	61 Pm —	62 Sm 150.43	63 Eu 152.0	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.27	69 Tm 168.93	70 Yb 173.05	71 Lu 174.97
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† The transuranium elements	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf
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PERIODIC TABLE (after Mendeleef)
(International atomic weights, 1952)

NORWICH SCHOOL
BOOK SLIP

[illegible]

THE ELEMENTS OF
PHYSICAL CHEMISTRY

A SCHOOL CHEMISTRY

Revision Notes and Questions

By F. W. GODDARD, M.A., F.C.S., and
S. R. HUMBY, M.C., M.A.

CHEMICAL ARITHMETIC

By F. W. GODDARD, M.A., F.C.S.

HIGHER CHEMICAL ARITHMETIC

By F. W. GODDARD, M.A., F.C.S.

A COMPLETE REVISION PHYSICS

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F. W. GODDARD, M.A., F.C.S.

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F. W. GODDARD, M.A., F.C.S.

A SCHOOL CHEMISTRY FOR TODAY

By F. W. GODDARD, M.A., F.C.S., and
KENNETH HUTTON, M.A., D.Phil.

THE ELEMENTS OF PHYSICAL CHEMISTRY

By

F. W. GODDARD, M.A., F.C.S.

(Formerly Senior Science Master, Winchester College)

AND

E. J. F. JAMES, M.A., D.Phil.

(High Master, Manchester Grammar School)

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PREFACE TO THE THIRD EDITION

FOR successive new impressions of this book errors and misprints have been corrected and small alterations have been made in the text to bring the subject-matter up to date.

For this new edition a more drastic revision has been undertaken in response to suggestions made by several experienced teachers of the subject.

Modifications in the accepted views on the existence of nuclear particles and the structure of the atom have been incorporated. Although the book is only intended to cover Sixth Form and first-year University courses, it has been thought advisable to include brief references to Dipole Moments, Hydrogen Bonds, Radioactive Disintegration and Nuclear Fission.

Diagrams showing the behaviour of solid and liquid mixtures have been improved and extended, and, by the addition of extra diagrams, the relationship between osmotic pressure and the depression of the freezing point, etc., has been clarified.

The chapter on Electrolysis has been rewritten to bring it into line with modern theory, and small additions have been made to the chapter on Colloids.

The questions at the end of the various chapters were originally carefully graded, and have been approved by various teachers and reviewers. These remain unaltered, but, to meet any demand for more modern questions of G.C.E. 'A' and 'S' level rather than of H.C. origin, more Miscellaneous Questions for revision purposes have been added at the end of the book.

The authors would like to take this opportunity of thanking readers who have kindly sent suggestions and at the same time to ask for more.

F. W. G.
E. J. F. J.

April, 1953.

PREFACE

THIS introduction to the study of Physical Chemistry is intended for the use of students preparing for Higher Certificate, First Medical, and University Entrance Scholarship Examinations. It is assumed that such students will have already acquired a knowledge of elementary physics and chemistry up to the standard of School Certificate or Matriculation.

It is of course undesirable, more especially in school science, to give the impression that the various branches of chemistry should be fitted into water-tight compartments; and yet most teachers find it convenient, during the post-certificate stage, to give a course of instruction labelled Physical Chemistry.

The growing importance of this branch of Chemistry in schools is shown by the fact that a sound knowledge of its principles is now necessary not only for students who intend to continue the study of Chemistry to an advanced stage, but also for medical students, physicists, and others whose chemical studies will end at Higher Certificate or possibly Pass Degree standard. This book attempts to meet the needs of both types of student. For the specialist it contains all the Physical Chemistry that is necessary for University Scholarship work. On the other hand, the anticipations of University 'Honours' work which are tending to creep more and more into school textbooks have been omitted, so that the medical student or Higher Certificate candidate should not be out of his depth.

The authors hope that this small textbook will serve a useful purpose in giving a concise account in logical form of the principles usually studied in such a course. We have aimed at presenting clearly the essentials only, for the teacher usually prefers to supply his own lecture demonstrations, anecdotes, and lantern-slide illustrations. Larger textbooks and original papers should in any case be consulted by the student from time to time. For this purpose a short bibliography has been added.

Two hundred and fifty questions have been graded and inserted at the conclusion of the appropriate chapters, and a small selection of miscellaneous examples for revision purposes has been added at the end of the book. These questions contain typical examples recently set by the various Examining Boards. We wish to acknowledge with gratitude the permission given to reprint these questions. Many of them involve calculations, for our experience shows that these are often the best test of thorough understanding of physico-chemical principles.

The sources of the examples are indicated as follows :—

Camb. Schol. . .	Cambridge Open Scholarship.
Oxf. Schol. . .	Oxford Open Scholarship.
Lond., H.C. . .	London Higher School Certificate.
N.U.J.B., H.C. .	Northern Universities Higher School Certificate.
Camb., H.C. . .	Cambridge Higher School Certificate.
Oxf., H.C. . .	Oxford Higher School Certificate.
O. & C., H.C. . .	Oxford and Cambridge Higher School Certificate.
C.W.B., H.C. . .	Central Welsh Board Higher School Certificate.
Camb., 1st M.B. .	Cambridge First Medical Examination.
Oxf. Prelim. . .	Oxford First Public Examination.

F. W. G.
E. J. F. J.

*The Science School,
Winchester College.
May, 1938.*

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CHAPTER I

THE ATOMIC AND MOLECULAR THEORY

The Laws of Chemical Combination.

THE study of chemistry in its quantitative aspect depends upon four fundamental laws: (1) *the Law of Conservation of Mass*; (2) *the Law of Constant Composition*; (3) *the Law of Equivalent Proportions*; (4) *the Law of Multiple Proportions*.

(1) *The Law of Conservation of Mass.*

This law states that *in a chemical change matter is never created or destroyed*. It must be realised that the truth of this law is tacitly assumed whenever a quantitative experiment is carried out, and its best proof lies in the constancy that is obtained in the results for any given determination. The law was first stated by Lavoisier in 1774, but definite experiments to test its accuracy were not carried out until this century, when several workers, notably Landolt (1906), examined the problem. The procedure adopted was to seal up two substances which react when mixed in the two limbs of a divided tube (Fig. 1). The tube and its contents are weighed as accurately as possible, and it is then shaken so that mixing and reaction occur. The tube is then again weighed. Among the reactions examined by Landolt in this way were those between silver sulphate and ferrous sulphate, hydriodic acid and iodic acid, and potassium hydroxide and chloral. In no case was any change in weight detected greater than 1 part in 10,000,000 parts, which was well within the limits of experimental error. Small losses in weight in experiments of this kind, observed by Heydweiler (1901), have been shown to be due to the heat given out during the reaction, which drives off the film of moisture which always condenses on glass, and which also

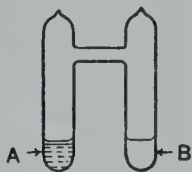


FIG. 1.—LANDOLT'S APPARATUS.

increases the buoyancy of the vessel by increasing its volume. Further confirmation of the law has been obtained by the still more accurate experiments of Manley (1907). Hence it may be stated that the Law of Conservation of Mass is true within the limits of a very small experimental error.

(2) The Law of Constant Composition.

This law states that *any compound always contains the same elements in the same proportions by weight*. Although quite fundamental to the study of chemistry, the truth of this law has been questioned several times. It was first enunciated by Proust in 1799, but was at once criticised by Berthollet, who based his objections firstly on the existence of 'compounds' such as glass, the composition of which may vary. It is now realised that such substances, although homogeneous, are in reality not compounds, but solutions. His second type of objection rested on such experiments as the oxidation of lead, in which various amounts of oxygen combine with the lead according to the conditions of the experiment. Berthollet's view was that lead and oxygen could, up to a certain limit, combine continuously. The true explanation, put forward by Proust, was that more than one compound of lead exists and that mixtures of these various oxides are formed, thus giving an appearance of inconstancy of composition, though each oxide in reality is of perfectly definite constitution. Thus Berthollet's objections to the law rest on an imperfect distinction between mixtures and compounds, and on the failure to allow for the existence of several different compounds between two elements. The positive proof of the law rests on the possibility of synthesising a single compound by a variety of methods, and subsequently showing by analysis that its composition remains unchanged. Thus if copper oxide, for example, is prepared by heating naturally occurring copper carbonate, artificial copper carbonate, copper nitrate or copper hydroxide, each of the specimens so obtained shows on reduction that it contains an identical percentage of copper. The most elaborate experiments to prove the law were those of Stas (1865), one of the first really accurate quantitative workers. Among his experiments may be mentioned the synthesis of silver chloride by a variety of methods, including direct combination, and precipita-

tion from silver nitrate by gaseous hydrogen chloride, by hydrochloric acid, and by ammonium chloride. In each case the weight of silver chloride obtained from 100 parts of silver was constant within the limits of experimental error, in this case about 1 in 100,000. The controversy concerning the truth of the law of constant composition served the purpose of stimulating more accurate quantitative methods, and also, from Berthollet's work, led to a fuller understanding of the effects of the concentration of reactants on the nature of chemical change.

(3) *The Law of Equivalent (or Reciprocal) Proportions.*

This law states that *the weights of two ^{ELEMENTS} substances A and B which are equivalent to a fixed weight of a third ^{ELEMENT} substance C are the weights in which A and B themselves react, or simple multiples of them.*

The meaning of this law may be made clear by a simple example. 12 gms. of magnesium are equivalent to 8 gms. of oxygen (*i.e.* these are the weights in which magnesium and oxygen combine) : 12 gms. of magnesium are equivalent to 1 gm. of hydrogen (in this case the magnesium displaces the hydrogen from an acid). The law of equivalent proportions states that 8 gms. of oxygen should combine with 1 gm. of hydrogen, and this is, in fact, the case. The importance of this law, which might be supported by an indefinite number of other examples, lies in the determination of combining weights, or *equivalents* (see pp. 9 ff.). The number of elements combining directly with hydrogen is limited, but nearly all elements combine with oxygen or chlorine. Since it is known that 8 gms. of oxygen or 35.5 gms. of chlorine combine with 1 gm. of hydrogen, the weights of elements combining with 8 gms. of oxygen or 35.5 gms. of chlorine having been determined, then by the law of equivalent proportions these are the weights which would combine with 1 gm. of hydrogen, or simple multiples of them.

(4) *The Law of Multiple Proportions.*

This law states that *if two elements, A and B form more than one compound, the weights of A combining with a fixed weight of B are in simple multiple proportions.*

This law was enunciated by Dalton in 1803, and it is probable that he derived it theoretically from his Atomic Theory (see later). Since then all the available evidence has supported the law. A

familiar example is provided by the oxides of copper. The weights of copper combining with a fixed weight of oxygen are found by reduction with hydrogen, and it is found that in cuprous oxide twice as much copper combines with a certain weight of oxygen as in cupric oxide. A more impressive example is provided by the oxides of nitrogen, since nitrogen and oxygen combine together in five different ratios. Their compositions are as follows :

Compound.	Parts Oxygen combining with 100 parts Nitrogen.
Nitrous oxide . . .	57
Nitric oxide . . .	114
Nitrogen trioxide . . .	171
Nitrogen dioxide . . .	228
Nitrogen pentoxide . . .	285

It will be seen that the parts of oxygen combining with a fixed weight of nitrogen are in the ratio 1 : 2 : 3 : 4 : 5, a striking confirmation of the law.

The Atomic Theory.

These laws of chemical combination are important not only because they summarise the fundamental facts about the quantities in which substances react, but also because they support a certain view of the constitution of matter. This view, the *Atomic Theory*, is of the most fundamental importance for the study of chemistry. It states that matter is not capable of infinite subdivision, for its structure is not continuous, all matter being built up of a very large number of particles or atoms. The four laws of chemical combination stated above become comprehensible and necessary if this view is adopted and if certain assumptions are made concerning the nature of atoms and their method of combination. These assumptions are as follows :

(1) All matter is made up of atoms, which are indivisible and indestructible particles. (The indestructibility of the atoms follows from the Law of Conservation of Matter.)

(2) All the atoms of a single element are identical but differ from those of any other element.

(3) Chemical combination takes place by a union occurring between one or more atoms of one element and one or more

atoms of another element, or of several other elements, the union always occurring between simple numbers of atoms. Thus if two elements A and B are combining, the compound formed is assumed to be AB_1 or AB_2 , or A_2B , or some similar simple structure.

It must be realised that the laws of combination are best explained by some such atomic hypothesis. The Law of Constant Composition suggests some discontinuity, since otherwise two elements would combine in any proportions, between certain limits. The Law of Equivalent Proportions makes this discontinuous structure almost certain, because it emphasises that substances combine in units of characteristic weight, which must presumably bear some relationship to the weights of their ultimate particles. The Law of Multiple Proportions suggests that atoms combine in simple numbers, for if A and B form more than one compound, those compounds will be AB , and AB_2 or AB_3 , or some other simple combination, from which it follows that the weights of B combining with a fixed weight of A will be in simple proportions. Dalton's theory made no distinction between 'atoms' of elements and 'atoms' of compounds. The idea of a *molecule* as the ultimate particle of a compound was only introduced with Avogadro's hypothesis (see later).

From Dalton's theory it follows that the *Atomic Weight* of an element is a most important quantity, since it is the weights of the atoms that finally determine combining proportions. Since the absolute weight of an atom is so small, and in any case was not ascertainable in Dalton's time, the atomic weight of an element is defined as the ratio of the weight of one of its atoms to the weight of an atom of hydrogen, hydrogen being chosen since it is the lightest known element. The advantages of defining atomic weights relative to oxygen as standard will be discussed later. In practice the atomic weight of an element is not usually directly ascertained, but rather the *equivalent weight*; that is, the weight which combines with or displaces unit weight of hydrogen. It must be emphasised that by Dalton's theory alone it is not possible to determine the atomic weight, because it is not known what multiple of the equivalent weight is the atomic weight. An example will illustrate this difficulty. The equivalent of oxygen is easily determined and is found to be 8. If Dalton's principle of

greatest simplicity is assumed the formula of water will be written HO. Since eight parts of oxygen combine with one part of hydrogen, and, on Dalton's assumption, one atom of oxygen combines with one atom of hydrogen, it follows that the atomic weight of oxygen is 8. If, however, water is made up of two atoms of hydrogen to one of oxygen, *i.e.* if water is H_2O , then the atomic weight of oxygen will be 16. Similarly if water is written H_3O , the atomic weight of oxygen will be 24, and so on. It is most important to realise that the simple atomic theory alone cannot decide between these alternatives. The combining power of an atom for other atoms is called its *valency*, which may be defined as the number of atoms of hydrogen with which one atom of the element combines. Thus in the three formulæ suggested above for water, HO, H_2O , H_3O , oxygen would be successively monovalent, divalent, and trivalent. It will be seen from this example that

$$\text{Atomic Weight} = \text{Equivalent} \times \text{Valency}.$$

Before atomic weights as distinct from equivalents could be determined, the atomic theory had therefore to be modified and elaborated. The most important new advance came from a study of the combination of gases, not as regards weight, but as regards volume.

In 1808 Gay-Lussac collected all the known examples of combinations between gases, and enunciated his **Law of Combining Volumes**, which states that *when gases combine, the volumes in which they do so bear simple proportions to one another and to the volume of the products if these are gaseous*. These volumes are of course measured under similar conditions of temperature and pressure. The law rests on such familiar observations as that one volume of oxygen combines with two volumes of hydrogen to give two volumes of steam. The law is now known not to be strictly accurate, but the small deviations are capable of satisfactory explanation. Since from Dalton's atomic theory it was assumed that the *numbers of atoms* of substances combining were in simple ratio; and from Gay-Lussac's generalisation it was clear that combining *volumes* of gases were in simple ratio, it seemed certain that there was a connection between the volumes of gases and the numbers of atoms they contained. At first the generalisation was

proposed that equal volumes of gases contain equal numbers of atoms. This, however, breaks down when we consider a simple example, such as the combination of hydrogen and chlorine. It is known that

1 volume of hydrogen combines with 1 volume of chlorine to yield 2 volumes of hydrogen chloride.

On the above provisional hypothesis it follows that

n atoms of hydrogen combine with n atoms of chlorine to give $2n$ 'atoms' of hydrogen chloride.

But each 'atom' of hydrogen chloride must contain at least 1 atom of hydrogen, the atom being *ex hypothesi* indivisible. Hence the absurdity is reached that n atoms of hydrogen can give a quantity of hydrogen chloride containing $2n$ atoms of hydrogen.

This paradox was resolved by **Avogadro's hypothesis** (1811), which modified the original atomic theory by introducing the conception of the *molecule*. While the atom was still regarded as the smallest particle of a substance capable of entering into chemical combination, the smallest particle capable of independent existence was called the *molecule*. Avogadro's hypothesis states that *equal volumes of all gases under the same conditions of temperature and pressure contain an equal number of molecules*. The importance of Avogadro's hypothesis was not immediately realised, but actually it fundamentally modified the views held by Dalton and his contemporaries. The first result that follows from it is the explanation of the difficulty encountered above by making it clear that the ultimate particles of hydrogen, chlorine, and other gases are not atoms, but molecules containing two or more atoms, H_2 , Cl_2 , etc. This result is apparent from the following reasoning.

1 vol. hydrogen + 1 vol. chlorine give 2 vols. hydrogen chloride.
Hence from Avogadro's hypothesis

n molecules hydrogen + n molecules chlorine give $2n$ molecules hydrogen chloride.

Since each molecule of hydrogen chloride must contain at least 1 atom of hydrogen, therefore:

n molecules of hydrogen must be equivalent to at least $2n$ atoms of hydrogen.

Hence the hydrogen molecule must contain at least 2 atoms, and the same is true for the chlorine molecule. Since hydrogen chloride forms only one series of salts (*e.g.* NaCl), it cannot be H_2Cl_2 , and hence the hydrogen molecule may be assigned the formula H_2 , and this is confirmed by other evidence. By considering other gas reactions it is found that oxygen, nitrogen, etc., consist of diatomic molecules.

The most important application of Avogadro's hypothesis to chemistry was made by *Cannizzaro* in 1858, who showed that the hypothesis provided the foundation for an easy method of determining the molecular weights of those substances which can be obtained as gases, and hence, as will be seen later, a valuable method for fixing atomic weights.

From Avogadro's hypothesis it follows that, since the density of a gas with respect to hydrogen

$$= \frac{\text{Weight of a given volume of the gas}}{\text{Weight of an equal volume of hydrogen}}$$

then the density

$$\begin{aligned} &= \frac{\text{Weight of } n \text{ molecules of the gas}}{\text{Weight of } n \text{ molecules of hydrogen}} \\ &= \frac{\text{Weight of one molecule of the gas}}{\text{Weight of one molecule of hydrogen}} \end{aligned}$$

Now, the weight of the hydrogen molecule is 2, if the weight of the hydrogen atom is taken as unity. Hence

The molecular weight of a gas $= 2 \times$ the density of the gas compared with hydrogen.

Hence Avogadro's hypothesis provides a method for the determination of the molecular weight of any substances which can be vaporised without decomposition.

This important principle may be put into another form as follows :

The volume occupied by n molecules of hydrogen $=$ the volume occupied by n molecules of any other gas (under similar conditions).

Hence, volume occupied by $2n$ gms. of hydrogen $=$ volume occupied by Mn gms. of any other gas of molecular weight M .

Hence the volume occupied by 2 gms. of hydrogen = volume occupied by M gms. of any other gas of molecular weight M .

It is found experimentally that 2 gms. of hydrogen occupy 22.2 litres at N.T.P. Thus the molecular weight in gms. of any gas occupies 22.2 litres at N.T.P. This '**gm. molecular volume**' of gases is usually taken as 22.4 litres, because oxygen is now taken as the standard of atomic weight.

The Determination of Equivalent Weights.

Avogadro's hypothesis, as has been said, is of the greatest importance for the determination of atomic weights. Before the

various methods for the determination of atomic weights can be discussed, however, it is necessary first to describe the methods available for the determination of *equivalent weights*, for it is usually the equivalent weight which is accurately determined, and so-called 'atomic weight

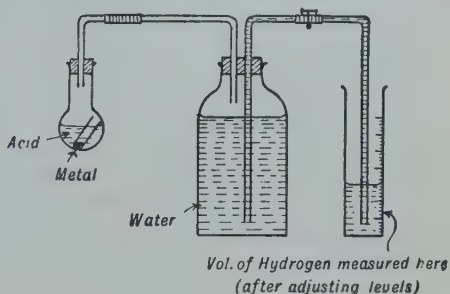


FIG. 2.

determinations' are really determinations of equivalent weight. The atomic weight is always a simple multiple of the equivalent weight, and if the atomic weight is *approximately* known, an accurate value may be obtained from an accurate knowledge of the equivalent. Very accurate determinations of equivalent weights therefore form an important part of quantitative chemistry.

1. The simplest method of determining the equivalent weight of an element, from the theoretical point of view, is to estimate the weight which combines with unit weight of hydrogen, or which displaces unit weight of hydrogen from acids or alkalis. The second method is only available for metals, and is not capable of a very high degree of accuracy, so that few of the classical determinations of equivalent weights have been carried out by this method. It is, however, very simple, and can be carried out in the laboratory using the apparatus shown in the diagram (Fig. 2).

A known weight of the metal is introduced into an appropriate acid (or alkali, with zinc or aluminium) by tipping the tube after the apparatus is closed. The volume of hydrogen given off is measured and corrected for temperature and pressure, whence the weight of hydrogen may be calculated.

The pressure inside the apparatus, both at the beginning and end of the experiment, should be atmospheric. Water is therefore poured into the cylinder until its level is the same as that in the Winchester. The clip on the delivery tube may then be closed and the cylinder emptied. When the hydrogen has displaced its equivalent volume of water into the cylinder the water level is again adjusted to that in the Winchester by raising or lowering the cylinder.

The method of direct combination with hydrogen has been used in one or two cases. Thus Dixon and Edgar found the equivalent weight of chlorine with great accuracy by burning hydrogen from a palladium bulb (weighed before and after use) in pure chlorine. The chlorine was prepared by the electrolysis of fused silver chloride, a method which gives the purest gas, and was weighed as a liquid in a sealed bulb. The hydrogen chloride formed was condensed in liquid air, and weighed directly, its weight thus giving a check on the weights of hydrogen and chlorine used.

2. A method of wider application is the determination of the equivalent with respect to oxygen, by conversion to oxide, a method which depends, of course, on the Law of Equivalent Proportions. A metal such as magnesium may be converted directly to oxide by burning in a stream of pure oxygen. With other metals (*e.g.* copper) it is necessary first to convert to the nitrate, which is then ignited to oxide. In the case of non-metals such as carbon or sulphur, the oxide is gaseous, and it is necessary to absorb it in some appropriate way before weighing. In the determination of the equivalent weight of carbon, for instance, a stream of pure oxygen is led over a known weight of carbon, which is heated in a combustion tube. The carbon dioxide which is formed is absorbed in weighed bulbs of potash.

Methods such as this depend upon an accurate knowledge of the combining ratio of hydrogen and oxygen. A special interest therefore attaches to the determination of this ratio. The first accurate work was that of *Dumas* (1842), who passed a stream of

purified hydrogen over a weighed quantity of copper oxide, the water formed being absorbed in weighed calcium chloride and phosphorus pentoxide tubes. Dumas prepared his hydrogen from ordinary zinc and sulphuric acid, but his purification of the gas was most elaborate. It was passed through U-tubes of lead nitrate (to remove hydrogen sulphide), silver sulphate (to remove arsine, etc.), caustic potash (to remove acid), sulphuric acid (to remove moisture), and phosphorus pentoxide (to complete the drying). Many of these tubes were duplicated. His precautions for absorbing the water formed were equally painstaking.

His value for the equivalent weight of oxygen ($H = 1$) was 7.98. This value has been shown to be inaccurate, since his method of purification of the hydrogen was inadequate, complex though it was. For example, passage of the hydrogen through concentrated sulphuric acid to remove water vapour actually introduced an impurity (sulphur dioxide) into the gas. The method of preparing a substance in an impure state and subsequently submitting it to a long course of purification is as far as possible omitted in modern work, and a method is sought by which the substance is obtained straight away in as pure a state as possible.

Morley's work is a classical example of a very accurate quantitative experiment. His method consisted of allowing weighed quantities of hydrogen and oxygen to combine directly, the water formed being also weighed as a check. Hydrogen and oxygen were

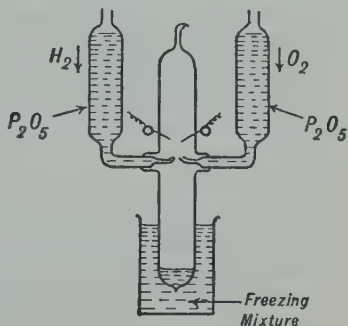


FIG. 3.—MORLEY'S APPARATUS.

weighed in large glass globes (the weighings being reduced to vacuo) and were passed from thence into the evacuated combustion vessel, where they were ignited by a spark at platinum jets (Fig. 3). The water formed was condensed in a freezing mixture, and its weight compared with the weights of hydrogen and oxygen used as determined by pumping off and analysing the residual gases from the combustion vessel. Morley's ratio was $1 : 7.9396$, or with oxygen as standard $1.0076 : 8$, the value now accepted.

In modern work with hydrogen and oxygen, the gases are prepared by electrolysis of baryta solution, the barium hydroxide having been repeatedly crystallised. The hydrogen is passed over potash and phosphorus pentoxide and is then absorbed in palladium, which has the property of absorbing, or 'occluding,' hydrogen, but not other gases. On heating the palladium, perfectly pure hydrogen is obtained.

3. The third method available for the determination of equivalents consists in the displacement of one element by another. Thus if a known weight of iron is placed in copper sulphate solution, copper is deposited and may be weighed. If the equivalent of one of the metals is known, that of the other is thus determined. The method has little practical importance.

4. A most important method is the analysis of the chloride of the element, by means of silver. The equivalent of sodium was determined by Richards, for example, by precipitating a known weight of the chloride, which can be obtained in a very pure state, with silver nitrate. The equivalents of silver and of chlorine are very accurately known, and hence the equivalent of the metal may be calculated either by weighing the silver chloride precipitated, or by observing the amount of silver nitrate required for complete precipitation.

5. A method of very wide application depends on the conversion of one compound into another, the equivalents of all but one of the elements involved being known. An excellent example of this may be found in the important work of *Stas* (1860), the pioneer of really accurate atomic weight determinations. *Stas* heated a known weight of potassium chlorate, and by weighing the potassium chloride left, he thus obtained the equivalent weight of potassium chloride. This potassium chloride was then precipitated with silver nitrate, and the silver chloride formed was weighed. The combining ratios of silver and chlorine he obtained by direct synthesis of silver chloride from its carefully purified elements, and also by precipitating silver chloride with pure ammonium chloride from a solution of a known weight of silver in nitric acid. By this series of experiments *Stas* established the following

ratios: $\text{KCl}:\text{O}$; $\text{KCl}:\text{AgCl}$; $\text{Ag}:\text{AgCl}$; $\text{Cl}:\text{AgCl}$, and hence determined the equivalents of silver, chlorine, and potassium. Although Stas' work was long considered a model of accuracy, there were, however, unsuspected sources of error which have necessitated subsequent correction. One such source of error may be mentioned. Stas always used considerable quantities of material, and consequently worked with concentrated solutions. It has been shown that when precipitation (*e.g.* of silver chloride) occurs in concentrated solutions, other salts are *adsorbed*, and the weight of precipitate is always too high. More recent workers (*e.g.* Richards in America, and Briscoe in England) have taken steps to eliminate this and other errors.

Errors in atomic weight determinations may arise from several other sources. Firstly, so called 'insoluble' substances may have a solubility sufficiently appreciable to affect the results. Secondly, a reaction may not proceed entirely in the direction assumed, but traces of by-products may be formed. Lastly, the substances used may not be perfectly pure. To eliminate this source of error, starting materials are usually prepared in several independent ways, and the greatest precautions are employed, some of which have already been mentioned.

•The Fixing of Atomic Weights.

The determinations which have been described have been those of equivalent weights. In Dalton's time there was no method of determining the atomic weight, as distinct from the equivalent, and as a result a number of Dalton's 'atomic weights' were erroneous. The following methods are now available for fixing the actual value of the atomic weight.

(1) *Dulong and Petit's Law.*

This generalisation was put forward in 1819. It states that *for all solid elements the atomic weight $\times$ the specific heat is equal to a constant, approximately 6.3*. The product of atomic weight and specific heat is called the **atomic heat**.

As an example of the application of this law we may take the case of copper. Copper forms two series of compounds, in which its equivalent is 31.75 and 63.5. From this it is clear that its atomic weight is 63.5 or 95.25, or 127, etc., *i.e.* some multiple of 31.75.

The specific heat of copper is approximately 0.09. By application of Dulong and Petit's law,

$$\text{Approximate atomic weight} = \frac{6.3}{.09} = 70.$$

Though this result is only approximate, it is sufficiently accurate to enable a definite decision to be made between the various possible alternatives in favour of 63.5 as the accurate atomic weight.

From the theoretical point of view the greatest interest attaches to the *exceptions*. Elements of low atomic weight and high melting point do not obey the law even approximately. The elements carbon (atomic weight 12, melting point above 2000°) and beryllium (atomic weight 9.02, melting point 1350°) are particularly noteworthy exceptions. Sodium, although of low atomic weight, has also a low melting point, and therefore obeys the law. It has been shown that if the specific heats of these exceptional elements are determined at high temperatures, values are obtained which are in agreement with the law. Similarly, if the specific heat of a 'normal' element such as copper is determined at very low

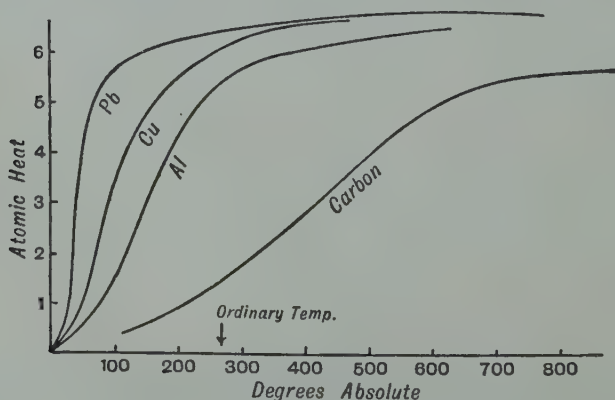


FIG. 4.—VARIATIONS IN ATOMIC HEAT WITH TEMPERATURE.

temperatures, its atomic heat becomes very small. The curves for the variation of atomic heat with temperature are shown in the diagram (Fig. 4) and it will be seen that for carbon the atomic heat only approaches the constant value at temperatures well above the ordinary. Beryllium and boron behave similarly.

Kopp showed that the atomic heat was an *additive property* in compounds; that is to say that the sum of the atomic heats of the elements in a compound gives a value nearly identical with the **molecular heat**, determined by multiplying the molecular weight by the specific heat of the compound itself. The law of molecular heat is not very accurate, but to some compounds it applies quite well. Thus for mercuric sulphide we have atomic heat of mercury = 6.38; atomic heat of sulphur = 5.22. Hence molecular heat of HgS (calculated) = $5.22 + 6.38 = 11.6$.

Molecular heat HgS (observed) = 232 (molecular weight) $\times$ 0.0517 (sp. heat) = 12.0.

(2) Cannizzaro's Method.

This method, which is of the greatest importance for the fixing of atomic weights, depends upon the deduction of Cannizzaro from Avogadro's hypothesis that the molecular weight of a compound is twice its vapour density with respect to hydrogen. The method simply involves the determination of the molecular weights and the analysis of as large a number as possible of the compounds of the element in question. It is highly probable that at least one of the compounds investigated will contain not more than one atom of the element. Hence it follows that *the atomic weight is taken as the least weight of the element occurring in the molecular weight of any of its compounds*. An example will illustrate this most important point. The following results are obtained with a number of compounds of carbon:

Compound.	V.D. (H=1).	M.W.	Parts of C in Molecular Weight.
Carbon monoxide .	14	28	12
Carbon dioxide .	22	44	12
Carbon disulphide .	38	76	12
Ethane . . .	15	30	$24 = 2 \times 12$
Ethylene . . .	14	28	$24 = 2 \times 12$
Acetylene . . .	13	26	$24 = 2 \times 12$
Benzene . . .	39	78	$72 = 6 \times 12$
Alcohol . . .	23	46	$24 = 2 \times 12$
Ether . . .	37	74	$48 = 4 \times 12$

It will be seen that the molecular weight of none of these compounds contains less than 12 parts of carbon. Hence if we assume

that some of them must contain only one atom of carbon, its atomic weight must be taken as 12. It must be emphasised that this assumption is only justifiable if we consider a large number of compounds. The greater the number of compounds examined the greater the probability that one at least of them contains only one atom of the element. Atomic weights determined by Cannizzaro's method thus have only a very great probability of being correct, but when taken in conjunction with other methods of confirming atomic weights the probability is so great that quite definite values are obtained. One particular point of importance in the method lies in the fact that it applies to just those elements to which Dulong and Petit's Law is either not applicable or for which anomalous results are obtained. Thus elements such as oxygen, nitrogen, and carbon all yield volatile compounds, whereas metals which do not usually form many such compounds may be dealt with by Dulong and Petit's Law.

Another application of vapour density determination to the fixing of atomic weights is found in the case of volatile chlorides. Here a process of trial and error sometimes yields information as to the correct multiple of the equivalent to adopt. For example, beryllium (equivalent 4.5) was for some time considered to be trivalent, and hence the atomic weight of 13.5 was ascribed to it. It forms few volatile compounds and does not obey Dulong and Petit's Law, so that this value, though criticised by Mendeléeff (see page 18), was accepted until it was found possible to determine the vapour density of beryllium chloride. This was found to be 40, giving a molecular weight of 80. This value for the molecular weight at once eliminated the possibility of there being three chlorine atoms in the molecule, for their weight alone would be 106.5. The possibility of only one chlorine atom being present was likewise eliminated, for if beryllium were monovalent, its atomic weight would be 4.5, and the molecular weight of its chloride 40. Hence this single molecular weight determination established the formula of beryllium chloride as BeCl_2 , fixing for beryllium a valency of 2, and hence an atomic weight of 9, the now accepted value.

Other methods of fixing atomic weights are of very limited application, but they have points of theoretical importance.

(3) *Mitscherlich's Law of Isomorphism.*

Although every crystalline substance forms crystals which are unique in character, the crystals of some substances are so similar in form that a crystal of one will be deposited round a crystal of the other suspended in its saturated solution. Such a formation is called an *overgrowth*. Thus if a crystal of chrome alum is suspended in a saturated solution of potash alum, the colourless potash alum will form a crystal round the purple chrome alum as a nucleus. A related phenomenon is the formation of *mixed crystals*. If a solution containing both potassium permanganate and potassium perchlorate is allowed to crystallise, the crystals deposited will contain both the compounds in quantities depending upon their relative concentrations. Substances so similar in crystalline form that they give overgrowths and mixed crystals are said to be *isomorphous*, and **Mitscherlich's Law** (1819) states that ***isomorphous substances have similar chemical constitutions***. The importance of this law for the determination of atomic weights lies in the help it gives in fixing the formulæ of compounds, and hence the valency of their constituent atoms. Thus potassium sulphate and potassium selenate are isomorphous. If potassium sulphate is known to be K_2SO_4 , then potassium selenate will be K_2SeO_4 , and the valency of selenium in this compound is therefore 6. If its equivalent is known, its atomic weight is thus fixed. The method has played little part in the actual determination of atomic weights, practically the only example being the fixing of the atomic weight of vanadium by Roscoe.

(4) *The Ratio of the Specific Heats of Gases.*

A gas has two distinct specific heats : that measured at constant pressure, the gas being allowed to expand during the heating process, and that at constant volume, in determining which no expansion is allowed to occur. These specific heats are usually denoted by the symbols C_p and C_v , respectively. Since in expansion a gas has to do external work against pressure, the amount of heat that has to be supplied to a gas to heat it through a given temperature range under constant pressure is greater than that if the volume is kept constant. Hence C_p is greater than C_v . It may be shown by thermodynamic reasoning (see, for example, Hinshelwood's *Thermodynamics for Students of Chemistry*) that

the ratio C_p/C_v will vary with the atomicity of the gas. For a monatomic gas this ratio will have the value 1.66, for a diatomic gas 1.41, and for a triatomic gas 1.28. If the vapour density of a gas be determined, its molecular weight is known, and from the ratio of its specific heats its atomicity, and hence its approximate atomic weight, may be found. The value will be only approximate, since vapour density determinations are not extremely accurate. Thus for mercury vapour, the density ($H = 1$) is 100, and the molecular weight is therefore 200. The ratio of the specific heats of mercury vapour is 1.66. Hence mercury exists as single atoms in the vapour, and its atomic weight = its molecular weight = 200. The practical determination of the ratio C_p/C_v is facilitated by the fact that it may be calculated from the velocity of sound in the gas.

(5) *The Periodic Classification.*

By arranging the elements in order of their atomic weights, Mendeléeff obtained a sequence in which various properties recurred at regular intervals. In this way he constructed the well-known *Periodic Table* (see Chapter II) in which elements showing a strong similarity in properties occur together in a group. The relevance of this arrangement for the fixing of atomic weights lies in the fact that if a wrong atomic weight is ascribed to an element, it will appear in the table in a group with which it has no similarities, *i.e.* its position in the sequence of the atomic weights will be a wrong one. Thus when beryllium was given the wrong atomic weight of 13.5, to which reference has already been made, there was no place for it in the table. It occurred between carbon (12) and nitrogen (14), whereas there was a gap in the table corresponding to its true atomic weight of 9. This method of fixing atomic weights has a usefulness in that it acts as a check upon other methods. But it has also led to some confusion and a good deal of fruitless redetermination of atomic weights, as, for instance, in the cases of argon and potassium, and iodine and tellurium, where the order of atomic weights is incorrect from the point of view of the periodic table, though the atomic weights are, in fact, accurate. The explanation of this anomaly lies in the conception of *atomic number*, which will be discussed later.

It has been said that atomic weights are now usually referred to the standard $O = 16$, rather than $H = 1$. This practice has

developed (1) since a much larger number of determinations can be made directly with regard to oxygen than with hydrogen, and (2) since the lightness of the hydrogen atom which made Dalton choose it as the standard is itself a disadvantage, because experimental errors become more significant. The old idea that hydrogen was the proper standard not only because of its lightness, but also because on the basis of $H = 1$ a large number of atomic weights come out to be whole numbers, has now been discarded, especially since the discovery of isotopes (see Chapter II).

The Determination of Vapour Densities.

As has been seen, the density of a substance in the gaseous state is a quantity of great importance from the point of view of the atomic theory. Considerable interest, therefore, attaches to the methods for determining vapour densities.

The Density of Gases.

The determination of the densities of substances which are gases at ordinary temperatures is a matter of some difficulty, but it is not, fortunately, nearly as important as the determination of the vapour densities of volatile liquids. For gases *Regnault's method* is used. This method involves weighing a bulb of known volume, first evacuated, and then filled with the gas. In order to compensate for the buoyancy of the bulb in air, it is counterpoised by another bulb of equal dimensions, which is kept evacuated. The temperature and pressure of the gas are noted and the density is corrected to N.T.P. A correction must also be applied for the change in volume of the bulb on evacuation, owing to contraction under atmospheric pressure.

The method has been applied to the measurement of the densities of very small quantities of gas (*e.g.* in work with the rare gases). The gas is contained in a small quartz bulb of known volume, and is counterpoised by a small quartz bead. The whole balance is enclosed in an air-tight metal case, oscillations of the beam being observed by a beam of light passing through a glass window in the case. Weighings are made by altering the pressure of air in the balance case, the pressure being registered on a manometer. The change in weight is calculated from the known change in buoyancy as the pressure is altered. By using a balance of this kind Ramsay was able to weigh less than 0.001 mgm. of material.

A more modern form of microbalance consists of a hollow quartz bulb of about 0.5 c.c. capacity which is evacuated. This is attached to a quartz beam which rests on a knife-edge.

The balance is enclosed in an air-tight case which has an entrance tube provided with a tap and fitted with a pressure gauge (Fig. 5(a)). The case is first filled with gas, whose density is required, at such a pressure that the balance beam becomes horizontal as viewed through a telescope. The case contains two plates as stops to prevent the beam from oscillating too far.

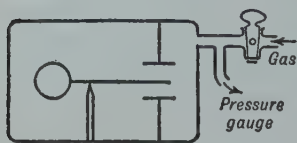


FIG. 5(a).

Secondly, the case is evacuated and then filled with oxygen, the pressure being adjusted until the balance beam is again horizontal.

When low pressures are used the gases obey Boyle's Law, and if p_1 and d_1 are the pressure and density of the gas used, p and d being the values for oxygen, then :

$$\frac{d}{p_1} = \frac{d_1}{p} \quad \therefore d_1 = d \times \frac{p}{p_1}$$

Vapour Densities of Volatile Liquids.

Three principal methods are available for the determination of the densities of the vapours of volatile liquids :

(1) Dumas's Method.

This method, like Regnault's method for gases, involves the weighing of a known volume of gas in a glass bulb. A bulb, usually of the shape shown in the diagram (Fig. 5b), is weighed 'empty'—that is to say, full of air. A quantity of the liquid under examination is then introduced into the Dumas bulb by alternately warming and cooling it. The bulb is then placed in a bath at a known temperature, which is well above the boiling point of the liquid (*e.g.* boiling water may be used for vapour density determinations with substances such as chloroform, b.p. 61°C. , or acetone, b.p. 57.5°C.). The liquid in the bulb boils vigorously, expelling the air, so that the bulb is finally completely filled with the vapour of

the liquid at the pressure of the atmosphere and the temperature of the heating bath. When it is quite certain that all the surplus vapour has been expelled, the end of the bulb is sealed off, the glass removed being, of course, preserved, so that it may be added to the bulb when it is next weighed. The bulb is now dried and allowed to cool, and is then re-weighed. Its volume is then determined by breaking the tip under water, when water enters and should completely fill the bulb. A weighing of bulb + water (together with the pieces of glass removed) gives the weight of water and hence the volume of the bulb. Since the volume and the weight of vapour under certain conditions of temperature and pressure are known, it is possible to calculate the density of the vapour as follows :

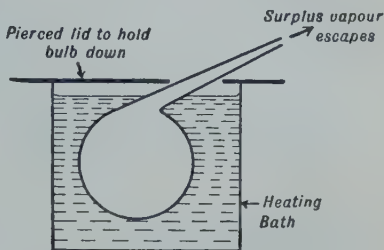


FIG. 5(b).—DUMAS'S METHOD.

Weight of bulb + air	= m
Weight of bulb + vapour	= M
Weight of bulb + water	= W
Barometric pressure	= p
Room temperature	= t_1
Temperature of bath	= t_2

The volume of the bulb = $W - m$ c.c. (The weight of air in the bulb may be neglected in this part of the calculation by comparison with the weight of water.)

Hence the volume of air in the bulb at N.T.P. would be

$$(W - m) \times \frac{273}{273 + t_1} \times \frac{p}{760}, \text{ and hence weight of air in bulb}$$

$$= (W - m) \times \frac{273}{273 + t_1} \times \frac{p}{760} \times 0.001293 \text{ gms.}$$

(since air has a density of 0.001293 gms. per c.c. at N.T.P.)

Hence weight of empty bulb

$$= m - \frac{(W - m) \times 273 \times p \times 0.001293}{(273 + t_1) \times 760} \text{ gms.}$$

Hence the weight of vapour in the bulb

$$= M - \left(m - \frac{(W - m) \times 273 \times p \times 0.001293}{(273 + t_1) \times 760} \right) \text{ gms.}$$

The volume of this vapour reduced to N.T.P. is

$$(W - m) \times \frac{273}{273 + t_2} \times \frac{p}{760}$$

Hence the density of the vapour is

$$\frac{M - \left(m - \frac{(W - m) \times 273 \times p \times 0.001293}{(273 + t_1) \times 760} \right)}{(W - m) \times \frac{273}{273 + t_2} \times \frac{p}{760}} \text{ gms. per c.c.}$$

This is usually divided by 0.00009 to obtain directly the vapour density with respect to hydrogen, 0.00009 gm. per c.c. being the density of hydrogen at N.T.P.

Dumas's method has two main disadvantages. It requires a fairly large quantity of the substance under examination; and secondly, if the liquid contains high-boiling impurities, it is those impurities which will be left in the bulb. Further, the method is not very accurate, as the weight of the vapour is always very small compared with the weight of the bulb. It has, however, two advantages. By using porcelain bulbs and a suitable heating bath, measurements may be taken at very high temperatures. Secondly, the method can be used for measuring the vapour densities of substances which dissociate on heating, since the actual volume of the vapour is known, and it is not diluted with an unknown volume of air as in Victor Meyer's method.

(2) Hofmann's Method.

This rather clumsy method is seldom employed. It consists in measuring the volume of a known weight of substance, under known conditions of temperature and pressure. The substance to be vaporised is accurately weighed in a very small stoppered bottle, and is introduced into a barometer tube (Fig. 6). This tube is jacketed by the vapour of a liquid boiling at a sufficiently high temperature to vaporise the substance, so that when the small tube floats to the top of the mercury, the liquid contained therein at

once vaporises, and if the barometer tube has been previously calibrated, the volume of the vapour may be read off directly. The temperature within the jacket is noted, and the pressure is that of the atmosphere minus the height of mercury in the barometer tube, correction being made if necessary for the effect of temperature on the density of mercury. If V is the volume of the vapour, t = the temperature, p = the pressure, and W = the weight of liquid, the density of the vapour at N.T.P.

$$= \frac{W}{V \times \frac{273}{273 + t} \times \frac{p}{760}} \text{ gms. per c.c.}$$

The only advantage that Hofmann's method possesses is that it may be used for liquids which decompose at their ordinary boiling points, since in a barometer tube the liquid vaporises much below its boiling point on account of the reduced pressure.

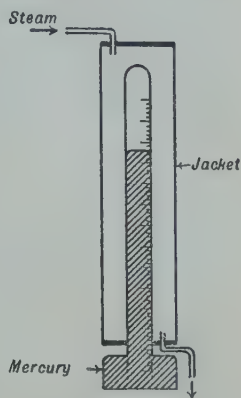


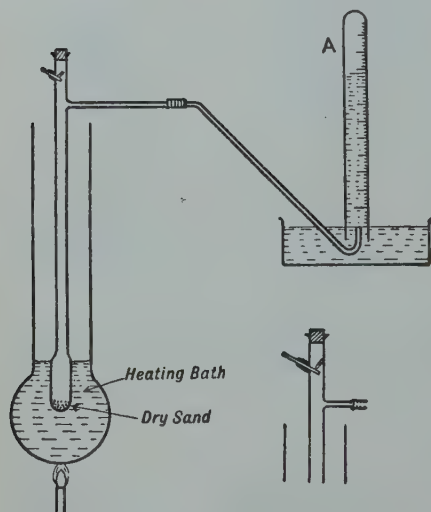
FIG. 6.—HOFMANN'S METHOD.

(3) Victor Meyer's Method.

The simplest and most generally adopted method for determining vapour densities is that of Victor Meyer. Here again the volume of a given weight of liquid is determined, but instead of the volume of vapour being directly measured, the volume of air displaced by the vapour is observed, and this may be carried out at room temperature and pressure. The apparatus used is shown in the diagram (Fig. 7).

The bath may be at *any* constant temperature above the boiling point of the substance, and one advantage of the method is that this temperature need not be known. A known weight of the liquid contained in a small bottle is introduced into the tube, and, before the experiment, rests on a glass rod passing through a small rubber tube as shown. When the air has finished expanding, and no more bubbles come off, the graduated tube *A* is placed over the delivery tube, the glass rod is moved so that the bottle falls to the bottom of the apparatus, and the liquid is then vaporised. The

volume of air displaced is finally read off, and the atmospheric temperature and pressure are noted. Since the air is collected over water, the pressure must be corrected for the tension of aqueous vapour at the temperature of the air. It must be realised that the volume observed is the volume of air displaced under room conditions, *not* the actual volume of the vapour at the



temperature of the bath. If V = the volume of air displaced and measured at temperature t and pressure p (the tension of aqueous vapour being h at $t^\circ \text{C.}$), the volume of vapour at N.T.P. would be

$$V \times \frac{273}{273 + t} \times \frac{p - h}{760} \text{ c.c.}$$

and the density, if W is the weight of substance taken, is

$$\frac{W}{V \times \frac{273}{273 + t} \times \frac{p - h}{760}} \text{ gms. per c.c.}$$

FIG. 7.—VICTOR MEYER'S METHOD.

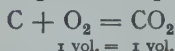
1. Victor Meyer's method has the advantage of great simplicity.
2. Further, it is not necessary to measure a high temperature.
3. Thirdly, a very small quantity of liquid may be used.
4. Lastly, by using a suitable apparatus a very high temperature may be employed. Its only limitations are that it cannot be used for substances which decompose at their ordinary boiling points; nor can it be used for substances which dissociate (*e.g.* phosphorus pentachloride), since their dissociation will be increased by dilution of the vapour with an unknown quantity of air.

The Molecular Formulæ of Gases : Gaseous Hydrocarbons.

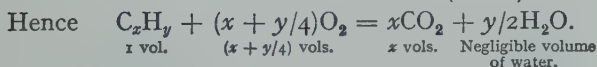
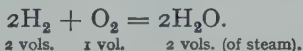
The molecular formulæ of gases are, in general, determined by a gravimetric analysis followed by a molecular weight determination. In some cases, however, notably the gaseous hydrocarbons,

it is possible to determine the molecular formula simply by observing the volume changes involved in their reaction with oxygen. The method is interesting as affording an exercise on Gay-Lussac's law and Avogadro's hypothesis, and also because it is of practical importance in determining the composition of gaseous mixtures. The procedure is to confine a known volume of the gas under examination in a eudiometer (in its simplest form a graduated tube containing wires for sparking, in which volumes of gases may be confined over mercury). A known volume of oxygen is introduced, and the mixture is sparked. Hydrogen (either free or in the hydrocarbon) is converted into water, of negligible volume, or, if the experiment is carried out above 100°C ., into steam. The carbon present in the hydrocarbon is burnt to carbon dioxide, and the volume of this gas formed may be determined by introducing potash, which completely absorbs it. The excess of oxygen may be absorbed in alkaline pyrogallol, though this is not usually necessary.

Suppose the formula of the hydrocarbon to be C_xH_y . Then, since carbon burns according to the equation



x atoms of carbon will yield x volumes of carbon dioxide. Also y atoms of hydrogen react with $y/4$ vols. of oxygen, since



The contraction on sparking is therefore

$$1 + y/4 \text{ vols.}$$

and a further contraction equal to x vols. of CO_2 will take place when potash is introduced.

Example.

7.5 c.c. of a gaseous hydrocarbon on combustion with 50 c.c. of oxygen gave a contraction of 22.5 c.c. When potash was introduced a further contraction of 22.5 c.c. took place, 12.5 c.c. of oxygen remained unused.

$$7.5 \text{ c.c.} = 1 \text{ vol.}$$

Then volume of $\text{CO}_2 = 22.5$ c.c. (by absorption in potash) = 3 vols.

Hence $x = 3$.

Contraction on sparking = 22.5 c.c. = 3 vols.

Hence $1 + y/4 = 3$

$\therefore y = 8$.

Therefore the molecular formula of the original hydrocarbon was C_3H_8 . *N.B.*—It is not necessary to know the volume of oxygen provided excess is used.

Abnormal Vapour Densities and Thermal Dissociation.

The vapour density of ammonium chloride, NH_4Cl , should be 26.75, since its molecular weight is 53.5. It was found by Deville (1866), however, that the actual value of the vapour density was 14.5, giving a molecular weight of approximately half the true value. This was at first thought to throw some doubt on Avogadro's hypothesis, but it was found that the true explanation was in the fact that, on heating, ammonium chloride splits up into ammonia and hydrogen chloride, the change being reversed on cooling, thus: $\text{NH}_4\text{Cl} \rightleftharpoons \text{NH}_3 + \text{HCl}$.

Hence it is the density of a mixture of ammonia and hydrogen chloride that is being measured. The phenomenon is known as **thermal dissociation**. That such a dissociation really does occur may be shown by separating the two gases in the vapour by



FIG. 8.—DISSOCIATION OF AMMONIUM CHLORIDE.

diffusion, as shown in the diagram (Fig. 8). A length of porous clay piping is enclosed in a wider glass tube, containing at one end some solid ammonium chloride. Heat is applied to the outer tube, the ammonium chloride vapour dissociates, and the ammonia, being the lighter product, diffuses through the porous pipe more rapidly than the hydrogen chloride (see Diffusion, page 56). A

slow current of air is passed through both tubes, with the result that the red litmus paper, *A*, turns blue and the blue litmus paper, *B*, turns red.

A similar abnormality is observed in the vapour density of phosphorus pentachloride, the dissociation



occurring. In this case the dissociation is qualitatively shown by the green colour of the vapour.

Similarly heating brings about dissociation of nitrogen tetroxide, N_2O_4 , into NO_2 molecules, with a corresponding diminution in vapour density and a colour change from pale yellow to dark brown.

Another interesting case of thermal dissociation is that of mercurous chloride, Hg_2Cl_2 . The vapour density of this substance agrees with the simple formula HgCl , but a piece of gold leaf placed in the vapour becomes amalgamated, showing that there is free mercury present. Baker found, however, that perfectly dry mercurous chloride gives a vapour density corresponding to the double formula, Hg_2Cl_2 , so that it is clear that under normal conditions the dissociation $\text{Hg}_2\text{Cl}_2 \rightleftharpoons \text{Hg} + \text{HgCl}_2$ occurs.

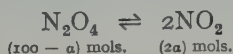
Baker also showed that perfectly dry ammonium chloride is also undissociated on heating and gives a normal value for the vapour density.

In the case of phosphorus pentachloride and similar thermal dissociations Wurtz showed that the addition of one of the products of dissociation, at constant volume, repressed the dissociation sufficiently for normal values of the vapour density to be found (see page 154).

Calculation of Degree of Dissociation from Abnormal Vapour Density.

The degree of dissociation is defined as the fraction of the original undissociated molecules which have broken down. This quantity is often expressed as a percentage.

For example, if we consider 100 mols. of N_2O_4 , under certain conditions of temperature and pressure a definite number of these, α , will have dissociated, according to the equation :



It will be observed that the dissociation of α mols. of N_2O_4 produces 2α mols. of NO_2 , leaving $(100 - \alpha)$ mols. of N_2O_4 undissociated. The resulting gaseous mixture will therefore contain $(100 - \alpha + 2\alpha)$, i.e. $(100 + \alpha)$ mols. of gas in place of the original 100 mols. From Avogadro's hypothesis it follows that the ratio :

$$\frac{\text{New volume of gas}}{\text{Original volume of gas}} = \frac{100 + \alpha}{100}.$$

Since the weight of gas is constant regardless of dissociation the vapour density must be inversely proportional to the volume occupied.

$$\text{Hence} \quad \frac{\text{Original Vapour Density}}{\text{New Vapour Density}} = \frac{100 + \alpha}{100}$$

$$\text{or } \alpha = 100 \frac{(\text{vapour density of } \text{N}_2\text{O}_4 - \text{vapour density of mixture})}{\text{vapour density of mixture}}.$$

In this case α is the percentage degree of dissociation.

Example.

The vapour density of phosphorus pentachloride, at 200°C . is found to be 70. Calculate the percentage degree of dissociation.

$$\text{Mol. wt.} \quad \text{PCl}_5 = 31 + (5 \times 35.5) = 208.5$$

$$\therefore \text{Vapour density, if undissociated} = 104.25$$



$$\begin{aligned} \frac{\text{New volume}}{\text{Vol. if } \text{PCl}_5 \text{ undissociated}} &= \frac{100 + \alpha}{100} \\ &= \frac{\text{Calculated vapour density for } \text{PCl}_5}{\text{Observed vapour density}} \end{aligned}$$

$$\therefore \quad \frac{100 + \alpha}{100} = \frac{104.25}{70}$$

$$\therefore \quad \alpha = 100 \left\{ \frac{104.25}{70} - 1 \right\} = \frac{34.25 \times 100}{70} = 48.9\%.$$

N.B.—The student is advised to carry out these calculations from first principles rather than to memorise a formula.

Note.—Students who have access to a good library might read with profit in connection with this chapter one or two original

papers dealing with atomic weight determinations, so that they may appreciate the difficulties involved and the precautions taken. Suggested papers are :—

Gray, *Journal of the Chemical Society*, 1905, **87**, 1601 (on the atomic weight of nitrogen).

Briscoe, *Journal of the Chemical Society*, 1915, **107**, 63 (on the atomic weight of tin).

Baxter and Bliss, *Journal of the American Chemical Society*, 1930, **52**, 4848 (on the atomic weight of lead).

QUESTIONS ON CHAPTER I.

1. State clearly (*a*) the law of multiple proportions, and (*b*) the law of reciprocal proportions (the law of equivalents). Illustrate your answer by using the analyses of the four following pure substances :

A Carbon 7.80%
Chlorine 92.20%

B Carbon 14.47%
Chlorine 85.53%

C Carbon 15.79%
Sulphur 84.21%

D Sulphur 47.44%
Chlorine 52.56%

(Lond. H.C.)

2. Discuss the law of constant combining proportions. Point out its bearing on the constitution of matter, and outline a method for examining its truth in any one case. (Camb. Schol.)

3. State Gay-Lussac's law of volumes, and give examples of reactions which illustrate this law. Explain how Avogadro's hypothesis is based on the law of volumes, and show that the vapour density of a volatile substance is one half of its molecular weight. (Camb. 1st M.B.)

4. Why do you believe in the correctness of Avogadro's hypothesis? (Oxf. Schol.)

5. Explain carefully how it comes about that (*a*) the atomic weight of an element divided by its equivalent equals a small whole number, and (*b*) the molecular weight of a substance is twice its vapour density. Define the terms employed. In your answer give *two* reasons supported by experimental evidence for believing that the molecule of hydrogen consists of two atoms. (N.U.J.B., H.C.)

6. Give an account of the fundamental theory of the determination of the molecular weight of substances in the gaseous state, and explain the bearing of these molecular weights on the problem of atomic weight determination. (C.W.B., H.C.)

7. The formula of water used at one time to be written HO. What was the foundation of this view, and why is the formula now written H₂O? (Camb. Schol.)

8. What are the conditions for the satisfactory determination of the equivalent weight of an element?

Show how far these have been fulfilled in the determination of the equivalent of any one element. (Oxf. Schol.)

9. How is it possible to determine the atomic weight of an element whose equivalent is known? Illustrate your answer by reference to the elements carbon and chromium. (Camb. Schol.)

10. (a) 1.00 gm. of the anhydrous sulphate of a metal, when heated, gave a residue of the oxide weighing 0.298 gm. The vapour density of the corresponding chloride was found to be 130 at low temperatures, but fell to about half this value at higher temperatures. The specific heat of the metal is 0.21.

(b) 100 c.c. of an elementary gas weigh 0.09 gm. at S.T.P. Its specific heat at constant volume is 0.15, and at constant pressure 0.25.

Calculate the atomic weights of the two elements, making use of all the data, and briefly explain the principles involved. (Proofs of a thermodynamical nature are not required.) (Oxf. H.C.)

11. The specific heat of a certain element varies with temperature, but attains a value of 0.054 at 300° . The element gives three oxides *A*, *B*, and *C*, which contain respectively, *A* 16.46, *B* 20.81, and *C* 24.72% of oxygen. Oxide *A* is volatile and at 1500° has a vapour density of 288 ($H = 1$), but on heating in air it passes into oxide *B*, which is non-volatile. Oxide *C* decomposes on heating to about 300° , yielding oxide *B*.

Calculate the atomic weight of the element and find formulæ for the three oxides. Express the changes indicated above by equations and explain any theoretical principles involved in your argument. (C.W.B., H.C.)

12. Describe methods by which the equivalents of *three* of the following elements might be ascertained: potassium, silicon, fluorine, sulphur.

State *one* method by which the atomic weight of each element chosen has been decided. (Camb. H.C.)

13. Explain fully the use of atomic heats and isomorphism in fixing the atomic weight of an element.

A crystalline solid which is isomorphous with potash alum contains water and the following, in percentages: a metal *X*, 23.41; aluminium, 4.75; sulphate radical, 33.80. The specific heat of *X* is 0.0482. Find the atomic weight of *X*. ($H = 1$, $O = 16$, $Al = 27$, $S = 32$.) (Lond. H.C.)

14. What is meant by the 'Principle of Isomorphism'? Give *two* examples of groups of isomorphous compounds and show how the principle may be used in determining the atomic weight of an element. Assuming that the atomic weight of calcium is 40.1, find the atomic weight of magnesium using the following data of percentage composition:

Calcium carbonate: $Ca = 40.06$; $C = 11.99$; $O = 47.95$.

Magnesium carbonate: $Mg = 28.91$; $C = 14.22$; $O = 56.87$.

(N.U.J.B., H.C.)

15. A metal m forms two sulphates which contain 63.16% and 72.00% of SO_4 , respectively. Calculate the equivalents of the metal, and the probable value for its atomic weight. Give an outline of the experiments which you would perform in order to confirm this value by consideration of isomorphous relationships, if you were provided with the two sulphates of m and also those of ammonium, magnesium, and aluminium. (Oxf. H.C.)

16. How would you determine the equivalent weight of iodine? How can it be shown that the equivalent and the atomic weight of this element are identical? (Camb. 1st. M.B.)

17. The specific heat of a metallic element, M , was found to be 0.0304, and when 0.898 gm. of its anhydrous bromide was heated in hydrogen, 0.418 gm. of the metal was left.

The specific heats of a gaseous element, G , were found to be 0.0385 at constant pressure and 0.0231 at constant volume, and 150 c.c. of the gas at 16°C . and 750 mm. pressure weighed 0.812 gm.

Explain briefly but clearly what conclusions you can draw about the elements M and G , and why.

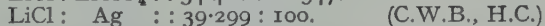
[Br = 80; 32 gms. of oxygen at S.T.P. occupy 22.4 litres.] (Oxf. Schol.)

18. The specific heat of a metal at 15°C . is 0.425. The metal forms a chloride which contains 88.65% of chlorine, and which has a vapour density of 40. Discuss the evidence for the atomic weight of the metal afforded by these data. (Camb. Schol.)

19. An oxide of an element contains 23.95% of oxygen and a chloride of the same element 45.61% of chlorine. Suggest an atomic weight for the element and write down a formula for the oxide.

Criticise the soundness of the method indicated above for the determination of atomic weights. (Camb. H.C.)

20. From the following experimentally determined ratios calculate the atomic weights of lithium, silver, and chlorine, taking the atomic weight of oxygen to be 16.00.



21. Explain how the atomic weight of sulphur could be determined accurately. (Camb. 1st M.B.)

22. Discuss the methods by which the atomic weight of an element, which does not form volatile compounds, could be determined. Illustrate your answer by examples. (Camb. Schol.)

23. The equivalent weight of a volatile metal is 100.3. The specific heat of the metal is 0.033. 0.25 gm. of the metal occupies 79.5 c.c. at 500°C . and 760 mm. Calculate the atomic weight of the metal and the molecular weight of its vapour. What value would you expect to find for the ratio of the specific heat of the metallic vapour at constant pressure to that at constant volume? (Camb. H.C.)

24. The vapour density of an anhydrous metallic chloride is 40. The sulphate of the metal crystallises with four molecules of water of crystallisation. 1.771 gm. of the hydrated sulphate on ignition yield 0.251 gm. of metallic oxide. Calculate the atomic weight of the metal. (Camb. Schol.)

25. 9.86 c.c. of a gas were mixed with oxygen so as to give a total volume of 104.5 c.c. After the explosion the total volume was unchanged. Aqueous potassium hydroxide removed carbon dioxide and left 74.92 c.c. of pure oxygen. Assign a molecular formula to the gas. (Camb. Schol.)

26. 25 c.c. of a mixture of methane, hydrogen, and carbon dioxide were exploded with 25 c.c. of oxygen in the presence of concentrated sulphuric acid, and the total volume decreased to 17.5 c.c. On treatment with potash solution the volume further decreased to 7.5 c.c. Calculate the composition of the mixture by volume. (O. & C., H.C.)

27. Describe the experiments you would make to estimate the proportions by volume of methane and hydrogen in a given mixture of these gases. Explain the reasoning you would use in calculating the result from the experimental data. (Camb. 1st. M.B.)

28. The carbide of a certain metal is decomposed by water, yielding a gas of which :

(a) 1 litre at S.T.P. weighs 0.405 gm.

(b) 20 c.c. exploded with 50 c.c. of oxygen in a eudiometer left, on cooling, a residue of 35 c.c., of which 10 c.c. were absorbed by potash, and the remainder by alkaline pyrogallol.

[All volumes are given as reduced to S.T.P. Weight of a litre of oxygen = 1.44 gm. O = 16.]

Show what conclusions can be drawn about the gas. If the metallic carbide contains 6.78% of carbon, what is the equivalent of the metal? (Oxf. Schol.)

29. A boiling tube drawn out to a jet at the open end weighs 52.30 gm. A small quantity of chloroform is drawn into the tube by heating and cooling. It is then placed in a bath of boiling water and sealed off, when no more liquid remains in the tube. The weight is now 52.63 gm. On opening the tube under water it fills and then weighs 177.7 gm. If the temperature were 15° C. and the pressure 750 mm. calculate the molecular weight of chloroform.

30. Describe, with an explanatory sketch of the apparatus, a method for determining the molecular weight of a volatile substance.

0.175 gm. of a volatile substance displaced 19 c.c. of air collected over water at 15° C. and 740 mm. pressure. What is its molecular weight?

[Pressure of aqueous vapour at 15° C. = 12.7 mm.] (Camb. H.C.)

31. The vapour density of nitrogen dioxide at 100° C. is 24.3. What conclusions can you draw from this experimental result?

32. Give examples of compounds showing abnormal vapour density. What explanation has been given to account for the abnormality, and what is the evidence for its correctness?

The density of nitrogen peroxide at 27°C . is 38.3. What is the composition of the vapour? (Camb. 1st. M.B.)

33. 'The molecular weight of any gas expressed in grams occupies 22.4 litres at N.T.P.' Explain how this statement is arrived at, knowing that 0.0899 gm. of hydrogen occupies 1 litre at N.T.P. Is it in agreement with the following facts, and if not, explain any discrepancies :

(a) 2 gm. of nitrogen peroxide occupy 1 litre at 70°C . and 760 mm.

(b) 1 gm. of phosphorus pentachloride when volatilised completely occupies 500 c.c. at 200°C . and 400 mm.

(c) 4.4 gms. of carbon dioxide at 273°C . and 380 mm. occupy 8.896 litres? (N.U.J.B., H.C.)

34. What do you understand by Dissociation? By what methods can the dissociation of a gaseous substance be recognised? The vapour density of phosphorus pentachloride at 250°C . and under atmospheric pressure is 57.6. What is the percentage dissociation of the compound under these conditions? (O. & C., H.C.)

35. What is meant by Thermal Dissociation? Give an account of the experimental evidence of thermal dissociation in the case of ammonium chloride.

Using a Victor Meyer apparatus, it was found that 0.0874 gm. of iodine displaced 13.7 c.c. of air measured at 21.5°C . and 723 mm. Calculate the vapour density of the iodine and the degree of dissociation at the temperature of the experiment. (Tension of aqueous vapour at 21.5°C . = 19.2 mm.) (Camb. 1st. M.B.)

CHAPTER II

VALENCY AND THE STRUCTURES OF ATOMS

IN the atomic theory of Dalton the atom was conceived as a solid indivisible particle, and for certain purposes this picture, as we have seen, was useful and satisfactory. It is now realised, however, that the atom is itself a complex structure, and the knowledge that has been obtained in the last thirty years concerning that structure has provided valuable information concerning the way in which atoms combine and a number of other physico-chemical problems. The lines of research which have led to this new conception of the atom are numerous. The study of X-rays, of spectra, and of radioactivity have all played a part, together with more specifically chemical lines of approach.

Electrons and Atomic Number.

At the end of the last century J. J. Thompson and others made the fundamental discovery of the existence of the electron by studying the discharge of electricity in high vacua, the term *electron* being used for the unit of negative electricity associated with a minute particle. It was found possible to determine the mass of this particle, and since it was found to be $1/1840$ of that of the hydrogen atom, the Daltonian conception of the indivisibility of the atom was at once discredited. Subsequent work showed that these electrons are constituents of the atoms of all elements. The work of Rutherford (1911) on the scattering of α -rays from radioactive substances went on to establish that the negative electrons in an atom surround a very small positive core or nucleus in which nearly all the weight of the atom is contained. Since atoms are electrically neutral the charge on the positive nucleus must be equal to that associated with the surrounding electrons. The important step of connecting this physical work with the chemical approach was carried out by Moseley in 1913. He showed that by bombarding elements with cathode rays, X-rays of characteristic wavelength are emitted. If the square roots of the frequencies of these waves are plotted against the '*atomic number*' straight lines are obtained.

The importance of this work was that it gave precision to the idea of atomic number which represents the order of the element in the Periodic Table, and avoided the anomalies (K, A; Te, I).

Moseley's Law established the conception that each element differs from the preceding one in the table by one nuclear charge, and hence by one electron. Thus by 1913 the nuclear theory of the atom was established. By this theory, to summarise its conclusions, the atoms of all elements are made up of a number of **electrons** which are particles of very small weight, each carrying a unit negative charge, surrounding a central nucleus which is positively charged. In this nucleus, practically the whole weight of the atom is concentrated. The constitution of the nucleus and the forces that hold it together are still the subjects of much research.

It is known that it is made up partly of **protons**, each of which carries a unit positive charge, and partly of **neutrons**, which have the same mass as protons but which are uncharged.

More recent research on cosmic rays suggests the existence of other nuclear particles, and in particular a **meson**. This has a mass of about 100 times that of the electron, and may be positively or negatively charged or uncharged.

The masses normally assigned to the protons and neutrons in an atom include the mass of the mesons.

Study of cosmic radiation has also shown the existence of a positive electron or **positron**. This has the same charge as a proton but is smaller.

Another probable nuclear particle is the **neutrino**, which has no charge and practically no mass. Since the atom is electrically neutral, the number of protons in the nucleus must equal the number of planetary electrons. The number of planetary electrons is called the atomic number and is the number of the element in the series of the elements arranged according to their atomic weights, the only exceptions being those cases where the order of chemical properties agrees with the atomic number rather than with the atomic weight. Thus, hydrogen has an atomic weight of 1, and an atomic number of 1, and hence consists of a central proton with one planetary electron. Sodium has an atomic number of 11 and an atomic weight of 23, and the sodium atom therefore is made up of 11 planetary electrons with a nucleus consisting of 11 protons to make the atom electrically neutral, and 12 neutrons to make up the weight.

Electronic Structure and the Periodic Classification.

From the point of view of the chemist the most important aspect of atomic structure lies in the arrangement of the planetary electrons round the central nucleus, for it is now known that the chemical properties of an element are entirely determined by this arrangement. The Periodic Classification of the elements taken in conjunction with the nuclear theory of the atom and the concept of atomic number has provided the information we now possess concerning the arrangement of the planetary electrons round the central nucleus. As Mendeléeff found, if the atoms are arranged in order of atomic weight, or (since the development of the electronic theory) in order of atomic number, a well-marked periodicity of properties occurs.

Thus the first eighteen elements are arranged as follows (the rare gases are included, though of course absent from Mendeléeff's original table).

			H					He
Li	Be	B	C	N	O	F		Ne
Na	Mg	Al	Si	P	S	Cl		A

Helium (atomic number 2), neon (10), and argon (18) are all rare gases, having the same inertness of character. Lithium (atomic number 3), and sodium (11), are both alkali metals with a striking similarity of properties. Thus for the first eighteen elements there is a repetition of properties (hydrogen excepted) if these elements are arranged in 'periods' of eight. After argon there is a period not of eight but of eighteen elements before the next rare gas, krypton, is reached, the *first long period* of the table, as it is termed, comprising the elements K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, and Kr. From krypton to xenon, the next rare gas, another long period occurs of eighteen elements (Rb, Sr, Y, Zr, Nb, Mo, Ma, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, I, Xe). Lastly, the table is completed up to the sixth rare gas (radium emanation) with a long period not of eighteen but of *thirty-two* elements, which includes the group of fourteen rare earths so similar in properties as to be included in one place in Mendeléeff's table. There is thus in the periodic table as now known a periodicity of properties occurring at intervals of 8, 8, 18, 18, and 32 elements. This periodicity of pro-

perties must be a reflection of some fundamental periodicity in atomic structure—that is to say, of the arrangement of the planetary electrons round the central nucleus, and the electronic theory about to be described was in part derived purely from a consideration of the chemical properties of the elements as reflected in the periodic table. The important point to realise, however, is that it also rests on the work of Bohr on spectra which has arrived at the same view of atomic structure quite independently of a consideration of the chemical properties of the elements.

The first two elements in the periodic table are hydrogen and helium, hydrogen having one planetary electron, helium 2. This orbit of two electrons is very stable, a fact reflected in the extreme

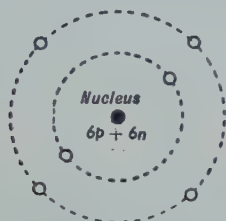


FIG. 9.—DIAGRAM OF CARBON ATOM.

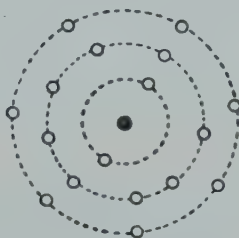


FIG. 10.—DIAGRAM OF CHLORINE ATOM.

unreactivity of helium. Between helium and neon there are eight elements, and in these elements there are two orbits—the first the complete inner orbit of two electrons, the outer one being built up one electron at a time, until with neon there is an outer ring of eight electrons. The stability of this structure is shown both mathematically and by the absence of chemical properties in neon. Thus the electrons in the first short period of the periodic table are arranged thus :

Li	.	.	.	.	.	2	1
Be	.	.	.	.	.	2	2
B	.	.	.	.	.	2	3
C	.	.	.	.	.	2	4
N	.	.	.	.	.	2	5
O	.	.	.	.	.	2	6
F	.	.	.	.	.	2	7
Ne	.	.	.	.	.	2	8

The structure of the carbon atom, as being typical, is shown in Fig. 9.

The next period of the table is likewise a short one, and here another stable outer ring of eight electrons is being built up, and is complete in the rare gas structure of argon, thus :

Na	.	.	.	.	2	8	1
Mg	.	.	.	.	2	8	2
Al	.	.	.	.	2	8	3
Si	.	.	.	.	2	8	4
P	.	.	.	.	2	8	5
S	.	.	.	.	2	8	6
Cl	.	.	.	.	2	8	7
A	.	.	.	.	2	8	8

The structure of the chlorine atom is shown in Fig. 10.

The next period is a long period, and its formation involves the building up of a ring of eighteen electrons which is apparently also a stable structure. After argon we have potassium and calcium, which apparently have normal structures, thus :

K	.	.	.	.	2	8	8	1
Ca	.	.	.	.	2	8	8	2

but the following elements as far as nickel show considerable differences from the elements preceding them in their groups. They have, moreover, certain properties in common. They all show variable valency, all have coloured ions, and all are paramagnetic. The spectroscopic evidence shows that in these *transitional elements*, as they are termed, the additional electrons, instead of going to build up the incomplete outer ring, go into the third orbit of the atom and make this up from 8 to 18, thus :

Sc	.	.	.	.	2	8	9	2
Ti	.	.	.	.	2	8	10	2
V	.	.	.	.	2	8	11	2
Cr	.	.	.	.	2	8	13	1 *
Mn	.	.	.	.	2	8	13	2
Fe	.	.	.	.	2	8	14	2
Co	.	.	.	.	2	8	15	2
Ni	.	.	.	.	2	8	16	2

Copper may have the structure 2, 8, 18, 1, which is known to represent cuprous copper, which is not transitional in properties, whereas cupric copper has the structure 2, 8, 17, 2, where the third orbit

* This structure for chromium is probably the correct one, but the student may find the ordinary chemical properties of chromium more comprehensible if thought of in terms of the structure 2, 8, 12, 2.

is still incomplete and the element is transitional. After copper we have zinc 2, 8, 18, 2 with no possibility of transitional properties, and the period is now completed in the usual way by addition of electrons to the outermost orbit until its full complement is reached with krypton, 2, 8, 18, 8.

The occurrence of a second long period and a second transitional group of elements within it is also due to a repetition of this process of building up an inner orbit to 18 rather than completing an outer orbit. Thus the structure of krypton is 2, 8, 18, 8, and that of xenon, the next rare gas, is 2, 8, 18, 18, 8.

In the next long period yet another process occurs. Not only is the fifth orbit made up to 18, making another transitional series, but the fourth orbit is built up from 18 to 32 electrons. The addition of these electrons to an orbit well within the atom has scarcely any effect on the chemical properties of the atom. Hence the fourteen atoms concerned, ranging from lanthanum 2, 8, 18, 18, 9, 2 to lutecium 2, 8, 18, 32, 9, 2, are all very closely similar in properties. They constitute the group of rare-earth elements which were such an anomaly in the periodic table before the electronic interpretation. Thus radium emanation, the last number of the rare-gas group, has the structure 2, 8, 18, 32, 18, 8.

It will be seen that the periodicity of the properties of the elements is based on a periodicity of atomic structure. Thus all the alkali metals have a single electron in the outer incomplete orbit, the inner orbits all being complete :

Li	.	.	.	.	2	1				
Na	.	.	.	.	2	8	1			
K	.	.	.	.	2	8	8	1		
Rb	.	.	.	.	2	8	18	8	1	
Cs	.	.	.	.	2	8	18	18	8	1

A study of atomic structure therefore makes the periodic table comprehensible, especially in view of the fact that the transitional elements and the rare earths fall into place in the scheme. Actually the interpretation of spectra has been carried much further by Bohr and others in the light of the quantum theory, and the electrons in any one orbit are now divided up into groups, but although this subdivision has chemical significance, it is of too difficult a character to be considered here.

Tables showing the Periodic Classification and the Arrangement of Electrons in the Atoms of the Elements will be found as end papers in this book.

Valency and Electronic Theory.

Among the properties of an element, its valency is one of the most important, and also one of those which is most clearly marked in the periodic table. It would be expected therefore that the electronic theory would be of use in considering the nature of valency, and in fact among the greatest triumphs of the electronic theory has been the light it has thrown on the way in which atoms combine.

The first theory of valency was that of Berzelius, put forward at the beginning of the nineteenth century. The theory was based entirely on inorganic compounds and ascribed all chemical combination to electrical forces. Some elements, such as sodium, iron, or sulphur, were positive in character and could combine by a process of neutralisation with negative elements such as oxygen or chlorine. In some of the resulting compounds neutralisation was incomplete, and a substance such as sulphur trioxide was still negatively charged and was capable of combining with a metal oxide which still retained a positive charge. This theory—the ***dualistic theory***—though adequate for most inorganic compounds, failed to explain the facts of the rapidly developing organic chemistry. Thus in many organic compounds the strongly negative chlorine could replace the positive hydrogen atom without a great change in the properties of the compound concerned. Attention became directed more and more towards carbon compounds, and valency was imagined simply as a link between atoms—different atoms being characterised by different numbers of links. The actual nature of the combining force was not considered. It was not until the end of the century that a clear distinction was drawn between ionisable compounds such as sodium chloride to which a modification of Berzelius' theory could apply, and non-ionisable compounds such as the majority of organic compounds to which the idea of electrostatic attraction was inapplicable.

Electrovalency.

The realisation that electrical forces were operative in forming chemical compounds made the application of electronic ideas possible. The conception that valency was due to a transfer of electrons was first put forward by Drude (1904) working on the

basis of Abegg's 'rule of eight,' which ascribes to an element two kinds of valency, positive and negative, which always add up to 8, the former being the number of the group in which the element occurs in the periodic table. Before the full relationship between valency and atomic structure could be cleared up, however, it was necessary that the arrangement of the electrons in the atom should be known, and hence the electronic theory of valency was not developed in a fuller form until the work of Lewis and of Kossel in 1916. These theories, though reasonably complete, were based on a static atom. After the work of Bohr, the electronic theory of valency as now held has been built up by Sidgwick and others on the basis of a dynamic atom.

A sodium atom is known to possess the electronic structure 2, 8, 1—that is to say, it has a single electron in an orbit outside two stable orbits. If a sodium atom loses this single electron it will become positively charged, and its electronic structure will be that of the rare-gas neon. Chlorine, on the other hand, with the structure 2, 8, 7, has only to gain one electron to become negatively charged and to acquire the structure of argon. Thus if an electron from a sodium atom is transferred bodily to a chlorine atom the resulting structures will have all the stability of rare-gas atoms. Sodium chloride therefore is formed by a transfer of this kind, and its stability is due to the stability of the rare-gas structures formed. A link of this kind involving the transfer of one or more electrons

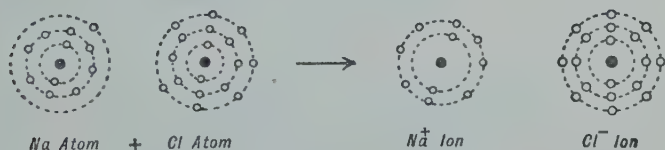


FIG. II.—COMBINATION OF SODIUM AND CHLORINE.

from one atom to another is called an **electrovalent** or **polar link** (see Fig. II).

The electronic theory thus explains several facts. The univalency of sodium is due to the possession of one outer or valency electron: the strongly metallic character of sodium is due to the readiness with which that electron is lost yielding a stable rare-gas structure. Further, the ionic character of sodium chloride is

shown by the charged character of the systems formed by the electron transfer. It is now known from the X-ray study of crystal structure that even solid sodium chloride consists of sodium ions and chlorine ions. Abegg's rule is now comprehensible, for in order to assume a rare-gas structure, an element may either lose n electrons (where n is its group number) or gain $8 - n$ electrons, though only very rarely does an ion possess more than three charges. The electronic explanation of the linkage in polar compounds also makes clear their physical properties. Bound together as they are by electrostatic attraction, it would be expected that these ions in the crystal lattice would be surrounded by strong fields of force which will prevent disruption. This is borne out by the fact that most salts are high-melting substances. Further, if an electrovalent compound is placed in a medium of high dielectric constant it would be expected that the charged ions would fall apart—a theoretical explanation of the fact that salts are soluble in water with resulting ionisation.

Covalency.

The electrovalency theory involving a complete transfer of electrons explains very satisfactorily such compounds as salts and oxides in which electrical forces have long been known to be at work. In order to explain the formation of the vast number of

non-ionised compounds, however, a new principle had to be introduced. If we consider the combination of carbon (2, 4) and chlorine (2, 8, 7) on electronic lines it will be seen that though four electrons could be transferred from a carbon atom to each of four chlorine atoms, another way is possible by which the carbon and chlorine atoms might all attain stable rare-gas structures. This is the method of **electron sharing**, by which the carbon atom shares two electrons with each of four chlorine atoms, as in the accompanying diagram (Fig. 12) in which

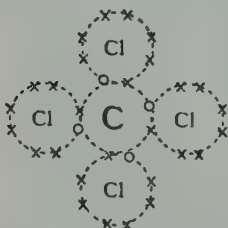


FIG. 12.—CARBON TETRACHLORIDE (ONLY VALENCY ELECTRONS ARE SHOWN).

dots represent carbon electrons, and crosses represent electrons from chlorine atoms.

A link of this type is spoken of as a **covalent link**. Com-

pounds such as carbon tetrachloride in which the formation of electrovalencies would involve the creation of highly charged atoms (with more than three charges) almost always have covalent structures. Although the actual mechanism of the sharing of electrons is obscure, it will be seen that in covalent compounds there are no definite electrical charges involved in holding the compound together, if we ignore the small charges produced by unequal sharing of the electrons. In carbon tetrachloride above, the carbon atom has lost a share in four electrons but it has gained a share in four others, so that it is still electrically neutral. Hence the assumption of covalent links explains the non-ionised nature of, for instance, the carbon compounds, which proved an insuperable difficulty to the dualistic theory. Further, since there are no electrical forces to hold covalent molecules together, they will usually be low-melting and low-boiling substances. In the solid state their crystals are held together only by weak intermolecular forces. The sharp distinction between chlorides such as sodium chloride, barium chloride, etc., which are high-melting substances, ionised in aqueous solution, and silicon chloride, stannic chloride, or even aluminium chloride, which are volatile substances, hydrolysed but not ionised by water, is comprehensible when it is remembered that the former group is electrovalent in character and the latter covalent. The stable character of the diatomic molecules of gases such as hydrogen and chlorine is explained by the existence of a covalent link between the atoms.

Dipole Moments.

A single atom is assumed to have the centre of action of its electrons coinciding with that of its positive nucleus. When it shares electrons with another atom, *i.e.* is combined with it by a covalent link, this sharing is not necessarily equal. If one atom takes a greater share of the two electrons, then this atom will have an excess of negative electricity associated with it, and the other atom will have a deficit. The centres of action of the negative and positive charges in the molecule will not then coincide, and may be represented by two-point charges separated by a distance d .

The product de is known as the **dipole moment** of the molecule.

Dipole moments can be calculated from the variation of dielectric constants with temperature or measured by a molecular beam method. Results so obtained throw considerable light on molecular structure.

Co-ordination.

Among the difficulties of the earlier theories of valency one of the greatest was the existence of what were variously known as 'complex compounds,' 'molecular addition compounds,' or 'co-ordination compounds.' Examples of these compounds are very numerous and are often of great importance in analytical and other work. Thus silver chloride dissolves in ammonia because it forms the compound AgCl_2NH_3 . Cupric hydroxide dissolves in ammonia forming the deep blue cuprammonium ion $[\text{Cu}(\text{NH}_3)_4]^{++}$. These are familiar examples of a large class of compounds—the amines (to be carefully distinguished from amines), formed by the addition of ammonia to neutral salts. The most stable are formed by transitional elements: thus chromium chloride treated with liquid ammonia yields chromium hexammine chloride $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$. Related to these are compounds such as potassium ferrocyanide and potassium ferricyanide $\text{K}_4[\text{Fe}(\text{CN})_6]$, $\text{K}_3[\text{Fe}(\text{CN})_6]$. These compounds are inexplicable on conventional valency lines. Werner explained their formation by imagining that the ammonia or other group was held by residual affinity, or '*co-ordinated*.' He drew attention to the fact that complex salts of the above types possessed an ionisable and non-ionisable portion. The co-ordinated groups are not ionisable, and this is represented by placing them inside a square bracket. Thus potassium ferrocyanide is said to be a complex salt because there are no ferrous or cyanide ions in its solution, but only potassium ions and ferrocyanide ions, thus:



This is the basis of the distinction between complex and double salts, such as alums, which in solution break up into all three constituent ions. Intermediate cases are known, however. Thus the detection of cadmium in the presence of copper in qualitative analysis depends on the fact that when potassium cyanide is added to a mixture of salts of these two metals the complexes $\text{K}_2[\text{Cd}(\text{CN})_4]$ and $\text{K}[\text{Cu}(\text{CN})_2]$ are formed. In the case of the cadmium complex there are, however, sufficient cadmium ions

present for hydrogen sulphide to precipitate cadmium sulphide. In the case of copper, owing to the greater stability of the complex ion, hydrogen sulphide produces no precipitate.

Werner's great contribution to the study of compounds of this

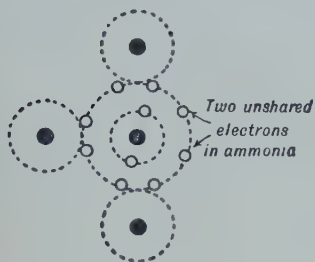


FIG. 13.—AMMONIA.

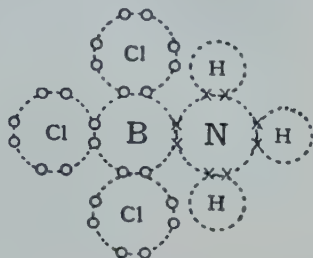


FIG. 14.—(SHOWING VALENCY ELECTRONS ONLY.)

kind was to introduce the idea of co-ordination and to show that the 'co-ordination number' of an atom—that is to say, the number of apparently saturated groups with which it could combine—was usually four or six. But the actual nature of the co-ordinate link was not elucidated until Sidgwick and others applied the electronic theory to its interpretation. The modern explanation consists of two postulates : firstly, that eight is not the only stable number for an outer ring of electrons but that rings of twelve or sixteen (and also ten) electrons may be formed*; secondly, that linkages of a covalent type can be formed by the sharing of two electrons in which both electrons are provided by one of the atoms. If the electronic formula for ammonia is examined (Fig. 13), it will be seen that there are two unshared electrons (a 'lone pair' as they are called). A share in these may be lent to another atom either with an incomplete shell, or with a shell capable of expansion. In such an arrangement the nitrogen is said to be the *donor* atom, and the other the *acceptor* atom. A simple example is found in the

* Sidgwick gives as the maximum covalency of an atom :

- (i) For hydrogen 2 (4 shared electrons).
- (ii) Lithium to fluorine 4 (8 shared electrons).
- (iii) Sodium to chlorine and potassium to bromine 6 (12 shared electrons).
- (iv) Rubidium to uranium 8 (16 shared electrons).

formation of the compound $\text{BCl}_3 \cdot \text{NH}_3$, which may be represented as in Fig. 14.

In the formation of an ammine such as $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$ the chromium atom starts with no valency electrons, these having been transferred to the chlorine atoms. The chromium ion acquires from each of six ammonia molecules a share in two electrons, giving it a moderately stable shell of twelve electrons (see Fig. 15).

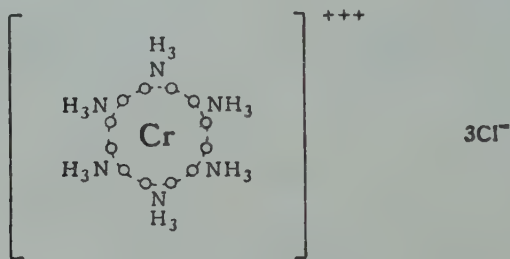


FIG. 15.

Other examples are too complex to be gone into here, but there is no doubt that the mechanism of co-ordination outlined above is on the right lines. Some writers refer to a *co-ordinate link* as a

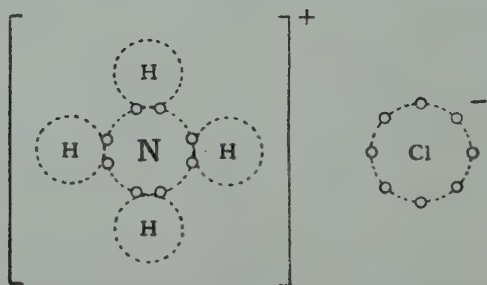


FIG. 16.—AMMONIUM CHLORIDE (SHOWING VALENCY ELECTRONS ONLY).

semipolar double bond. This is because it possesses the properties both of a covalent link (for electrons are shared in its formation) and of an electrovalent link, for by losing a share in two electrons the donor atom acquires a positive charge.

Only two further examples need be given of the application of

the electronic theory to the formulation of well-known compounds. Ammonium chloride is formed by the combination of ammonia and hydrogen chloride. This may be regarded as the donation of a share in its two unshared electrons by the nitrogen atom to a hydrogen ion which thereby takes up the stable helium structure. The formula of ammonium chloride is therefore as shown in Fig. 16.

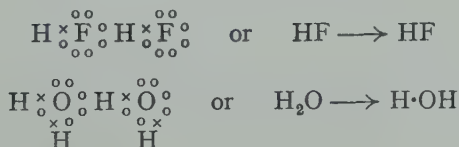
The important point to realise here is that in ammonium chloride, nitrogen is not merely 'pentavalent.' It is more correct to say that it has a *covalency* of four and the resulting structure has an *electrovalency* of one. This emphasises the difference between four of the nitrogen valencies and the fifth.

The Hydrogen Bond.

Many of the physical properties of water such as its high boiling point, high surface tension and dielectric constant indicate that it is associated into $(\text{H}_2\text{O})_2$ and $(\text{H}_2\text{O})_3$ molecules.

Similarly, experiments on the vapour density of hydrogen fluoride and its effect on the freezing point of water suggest the double formula H_2F_2 . There seems to be no doubt that it gives the ion $[\text{F}-\text{H}-\text{F}]^-$.

Hydrogen would appear to have a valency, in such compounds, of 2 and to be capable of forming a stable ring of four electrons thus :



This interaction between a hydrogen atom and other atoms (such as O, N, F, Cl), especially when it is present as an OH or NH group, is now regarded as due to a 'hydrogen bond'; an electrostatic effect of the single proton in the hydrogen atom.

Singlet Linkage.

In addition to the types of linkage mentioned above, it is possible that links consisting of a single shared electron exist.

They have been used to formulate compounds such as boron

hydride, B_2H_6 , $H \overset{\times}{\underset{\times}{\underset{\times}{B}}} \overset{\times}{\underset{\times}{\underset{\times}{B}}} H$, which are otherwise difficult to

explain. Another possibility is $\left[\begin{array}{c} H \\ \diagdown \\ B \\ \diagup \\ H \end{array} = \begin{array}{c} H \\ \diagup \\ B \\ \diagdown \\ H \end{array} \right]^{--} 2H^+$.

It must be realised, however, that modern theories of valency in terms of quantum mechanics are based on views of the sharing of electrons which are both less simple and less mechanical than those described here.

Isotopes.

It is remarkable that the atomic weights of a large number of elements are very nearly whole numbers, this being true of a much greater number of elements than can be explained merely on a basis of probability. *Prout* (1815) in fact put forward as a hypothesis that the atomic weights of all elements were really whole numbers, but successive determinations of the atomic weight of chlorine, for example, (atomic weight 35.46), failed to confirm this view. A consideration of atomic structure shows, however, that *Prout's* hypothesis had a foundation in fact. Since all elements are built up of identical protons, neutrons and electrons (nearly all the weight being concentrated in the protons and neutrons), it would be expected that the atomic weights of all elements should be simple multiples of that of hydrogen. The explanation of the fact that this is not the case is to be found in the existence of *isotopes*. It has been said that the chemical properties of an atom depend entirely on the planetary electrons. Hence if the nucleus is increased by one neutron, the chemical properties of the element remain absolutely unchanged. Its atomic *number* is also unaltered, so that its position in the periodic table also remains the same, although the atomic *weight* is now different. Hence we have two elements of identical chemical properties but different in atomic weight. Such elements are known as *isotopes*. Boron, for example (atomic number 5), may have either of the structures shown in Fig. 17.

These isotopes may be represented as $^{10}_5B$ and $^{11}_5B$, the upper figure being the atomic mass, the lower one the atomic number.

Actually boron is a *mixture*, quite inseparable by chemical

means, of these two isotopes. Hence its atomic weight is 10.82, since the heavier isotope predominates.

It has been shown in recent years (mainly by Aston, whose book "Isotopes" should be consulted for further information), that nearly all elements consist of mixtures of two or more isotopes. Thus when an element is obtained in the laboratory it is really a mixture that is obtained, but this mixture when prepared artificially is invariable in composition, and hence the atomic weight of the element is constant. It is useless to attempt to separate isotopes chemically, for their chemical properties are completely identical, though their physical properties (*e.g.* density) may differ very slightly, and it has been possible in some cases to effect a partial separation by making use of these differences. The deviation of atomic weights from whole numbers is thus explained.

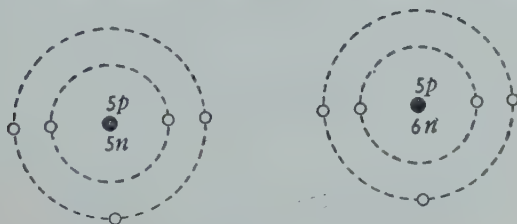


FIG. 17.—ISOTOPES OF BORON.

Chlorine is known, for instance, to consist of isotopes with atomic weights of 35, 37, and 39. Prout's hypothesis has, therefore, been reinstated in a modified form. It is of particular interest to note that hydrogen itself has two isotopes, ${}^1\text{H}$ and ${}^2\text{H}$ (of masses 1 and 2), these being exceptional in that they do differ slightly in chemical properties, and also in their ease of separation. Further, in recent years a considerable amount of work has been carried out on *heavy water*, this being water containing the heavier isotope of hydrogen.

The proved existence of heavy hydrogen, ${}^2\text{H}_2$, has bearing on the fixing of atomic weights. If these are stated on the scale ${}^1\text{H} = 1$ it is most important that the experimental results which determine them should refer to pure hydrogen and not to a mixture of ${}^1\text{H}_2$ and ${}^2\text{H}_2$ as is obtained in electrolytic gas.

Oxygen has three isotopes 16, 17, 18, but in ordinary oxygen

the proportion of the two higher isotopes is very small, and so $\alpha = 16$ (*i.e.* the ordinary mixture of isotopes) is still taken as the standard for fixing atomic weights.

Radioactive Disintegration.

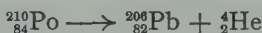
Details of this subject are to be found in the physics textbooks, but a brief summary will not be out of place here.

Certain elements such as uranium, thorium and actinium disintegrate into other elements, and in doing so give out rays. These rays are of three types :

1. α -Particles which are helium atoms which have lost both planetary electrons. Thus when an atom such as radium loses one α -particle it becomes radium emanation or radon, which will be an element two places to the left of radium in the Periodic Table and having an inert-gas structure. The helium nucleus contains two protons and two neutrons, and so the radium atom, in losing an α -particle, loses four units of mass. The two planetary electrons, no longer attracted by the protons which were in the nucleus, are set free.

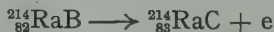
The α -particle (helium nucleus) later picks up two planetary electrons, and becomes a helium atom.

Similarly, polonium emits an α -particle and becomes lead.



2. β -Particles are electrons radiated *from the nucleus*. It would appear therefore that in unstable atoms some neutrons are made up of protons and electrons. The loss of one electron from the nucleus does not appreciably alter the atomic mass, but it does leave in the nucleus an excess of one positive charge, an extra planetary charge is therefore attracted into the orbits from the surrounding space.

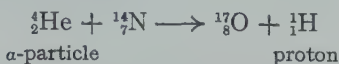
Thus radium B (an isotope of lead) becomes radium C (an isotope of bismuth), which occupies one place farther to the right in the Periodic Table.



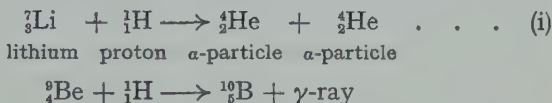
3. γ -Rays which are X-rays of high frequency and which often accompany the emission of β -particles have neither charge nor mass.

Thus radioactive elements transmute themselves as a result of spontaneous changes in the nucleus.

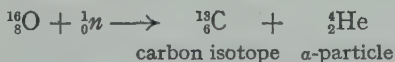
Transmutations may also be obtained by the bombardment of atoms by nuclear particles. The first experiment of this type was performed by Rutherford in 1919 when he obtained charged hydrogen nuclei or protons by bombarding nitrogen with fast-moving α -particles from radium.



Protons can also be used for these bombardments, provided they are given sufficiently high speeds. This is done by passing them over and over again through a high-potential field in a **cyclotron**. In this way the following disintegrations have been performed :



Neutrons have also been used : They are more effective but more difficult to produce.



The nucleus of the hydrogen isotope ${}^2_1\text{H}_1$ deuteron, can convert nitrogen into carbon



Atomic Energy.

In equation (i) above the total mass of the right-hand side is less than that of the left-hand side; *i.e.* the conservation of mass does not apply. This disappearance of mass does, however, mean a release of energy according to Einstein's equation

$$E = mc^2$$

in which E is the energy, m is the mass and c is the velocity of light.

So much energy is required to speed up the protons sufficiently to bombard effectively the lithium nucleus that equation (i) does not lead to a profitable production of atomic energy.

Nuclear Fission.

When the lighter elements are bombarded with *neutrons*, nuclei of larger atomic number are obtained.

With uranium, however, the nucleus breaks down, giving elements with lighter nuclei such as barium, strontium, iodine, etc.

The uranium nucleus, having taken in a neutron, immediately breaks down into two parts with the evolution of much energy and some neutrons. Each of these in turn can bombard another uranium nucleus, setting up a chain reaction.

Natural uranium consists of several isotopes, but U_{235} is the one which gives the effective chain reactions, and is only present to the extent of 0.7 per cent. in the natural uranium. Speeds of neutrons can be adjusted by passing them through certain lighter elements (*e.g.* pure graphite) so as to increase the chances of their being captured by U_{235} rather than by other isotopes.

The plutonium isotope Pu_{239} also shows nuclear fission. U_{235} and Pu_{239} have thus been used in *atomic bombs*.

For these the mass of material which can undergo fission has to be of such a size that the production of free neutrons by fission is equal to the loss of neutrons by escape and to other atoms. When atomic explosion is required two portions of material are put into contact so that together they give the correct size.

When arranged with graphite and cadmium strips to control the number of neutrons, rods of uranium can be built into an *atomic pile*.

The energy released as the result of nuclear fission can thus be utilised as a source of power. It is estimated that, weight for weight, uranium will be from two to three million times as effective as coal.

QUESTIONS ON CHAPTER II.

1. Write a brief essay on 'the modern theory of atoms' and its relation to the periodic classification of the elements. (C.W.B., H.C.)

2. Explain the various types of valency from the standpoint of atomic structure. How would you account for the differences between an ionisable and an unionisable bond? (Camb. Schol.)

3. Explain the various types of valency from the standpoint of atomic structure. Illustrate your answer by the electronic structure of methane, ammonia, and ammonium chloride. (Camb. Schol.)

4. The atomic weight of zinc is 65 and its atom is bivalent. These data suffice to indicate the place of zinc in the classification of the elements. But a clearer indication is given by the statement that the atomic number of zinc is 30. Explain and amplify. (Oxf. Schol.)

5. The elements of the second period of the Periodic Classification, their atomic weights and atomic numbers, are given below :

	Na	Mg	Al	Si	P	S	Cl	A
Atomic Wt. .	23.0	24.3	27.0	28.0	31.0	32.0	35.46	39.94
Atomic No. .	11	12	13	14	15	16	17	18

Explain the typical valencies exhibited by these elements from the standpoint of atomic structure. What explanation is given for the fact that the atomic weight of chlorine is not approximately a whole number? (C.W.B., H.C.)

6. Discuss the valency of nitrogen in the following compounds: ammonium chloride, nitrobenzene, nitrogen trichloride, and 'cuprammonium' sulphate (tetrammine-copper sulphate). (Oxf. Schol.)

7. Write a short essay on **one** of the following :

(a) Valency.

(b) The structure of the atom.

(Oxf. Schol.)

CHAPTER III

THE GASEOUS AND LIQUID STATES

OF the three states of matter, the gaseous state is by far the easiest to examine accurately, and the laws governing the behaviour of gases are of the greatest importance. The condition of a gas depends upon three variables: the pressure, the volume, and the temperature. The simplest law connected with gases is that law which connects the pressure and the volume of a gas, the third variable, temperature, being kept constant. This is **Boyle's Law**, and it states that *for a given mass of gas the volume is inversely proportional to the pressure if the temperature remains constant*; or

$$pv = k$$

Thus if the product pv is plotted vertically against the pressure horizontally, a horizontal straight line should be obtained if Boyle's Law is correct. Such a curve is spoken of as an **isothermal**. In actual fact, as will be shown, isothermals are not perfectly straight lines, owing to deviations from Boyle's Law.

The variation of the volume of a gas with the temperature is summarised in **Charles' Law**, which states that *the volume of a given mass of gas increases (or decreases) by $\frac{1}{273}$ of its value at 0°C . for each degree centigrade rise (or fall) in temperature, the pressure being kept constant throughout*. Thus

$$v_t = v_0 \left(1 + \frac{t}{273} \right)$$

where v_t is the volume at a temperature $t^{\circ}\text{C}$., and v_0 is the volume at 0°C . At -273°C . the volume of the gas would obviously be zero if the contraction continued to obey this law at the lowest temperatures, and if the gas did not liquefy. The temperature -273°C . is the *absolute zero*. From the above equation

$$v_t = v_0 \left(1 + \frac{t}{273} \right)$$

it follows that

$$v_t = \frac{v_0(t + 273)}{273}$$

$t + 273$ is called the *absolute temperature*, that is, the temperature

expressed on a scale with the absolute zero as 0° . The values of temperatures on the absolute scale are obtained by adding 273 to the corresponding temperatures on the centigrade scale. If we write the absolute temperature as T , the above equation becomes:

$$v_t = \frac{v_o T}{273}$$

or

$$V = kT,$$

that is to say, the volume of a given mass of gas at constant pressure is proportional to the absolute temperature.

From Boyle's Law and Charles' Law it follows that if the volume is kept constant and the temperature is increased, the increased pressure is given by

$$p_t = p_o \left(1 + \frac{t}{273} \right)$$

or

$$P = kT,$$

that is to say, the pressure of a given mass of gas at constant volume is proportional to the absolute temperature.

There are thus three equations governing the behaviour of gases with variations of the three variables pressure volume, and temperature, each law applying to the case in which one of the three is kept constant. These three equations may be combined in one general **Gas Equation**, thus:

Let the pressure and volume of a given mass of gas at 0° C. be p_o and v_o . If the pressure of the gas is changed to p_1 , the temperature remaining constant, then by Boyle's Law

$$p_1 v = p_o v_o$$

If the same given mass of gas is now heated to t° C., the pressure remaining at p_1 , then the new volume v_1 is given by

Charles' Law as: $v_1 = v \left(1 + \frac{t}{273} \right)$

$$\therefore p_1 v_1 = p_1 v \left(1 + \frac{t}{273} \right) = p_o v_o \left(1 + \frac{t}{273} \right)$$

$$\text{or } \frac{p_1 v_1}{T_1} = \frac{p_o v_o}{T_o} \text{ where } T_1 = 273 + t$$

or, in general terms, the pressure, volume and absolute temperature of a gas are related by the equation

$$pv = kT$$

It will be seen that if in this equation the temperature is constant, the general form becomes $p v = k$, or the form becomes that of Boyle's Law. Similarly if p or v is kept constant, then $v = kT$, or $p = kT$ respectively, *i.e.* the general Gas Equation becomes the expression of Charles' Law.

The value of k in the gas equation depends on the units in which p and v are measured, and on the mass of gas considered. If 1 gm.-molecule of the gas is considered, however, the constant is the same for all gases, for Avogadro's hypothesis states that 1 gm.-molecule of any gas occupies a constant volume at N.T.P., *i.e.* 22.4 litres. The equation, when applied to 1 gm.-molecule of a gas, is usually written

$$PV = RT$$

If P is expressed in atmospheres, and V in litres, we have

$$\begin{aligned} 1 \times 22.4 &= R \times 273 \\ \text{or} \quad R &= 0.082 \end{aligned}$$

The units in this case are litre-atmospheres per ° C. If P and V are expressed in c.g.s. units (*i.e.* pressure in dynes per sq. cm. and V in c.c.s.)

$$\begin{aligned} R &= \frac{76 \times 13.6 \times 981 \times 22,400}{273} \\ &= 8.3 \times 10^7 \text{ ergs per degree} \end{aligned}$$

or, since 1 calorie = 4.18×10^7 ergs.

$$R = \text{approximately } 2 \text{ calories per degree.}$$

It will be seen that R is in units of work per degree.

The gas laws so far considered are purely empirical, and are independent of any view as to the structure of gases. It is, however, of great value to consider gases from the point of view of the molecular hypothesis, when we obtain a picture of gases that is referred to as the **Kinetic Theory of Gases**. This theory, which considers gases as made up of molecules in constant movement at considerable distances one from another, receives support from a study of the diffusion of gases.

Gaseous Diffusion.

The phenomenon of gaseous diffusion is very readily demonstrated by the rapidity with which a heavy gas such as nitrogen

dioxide or bromine vapour fills any space into which it is introduced. A gas with a characteristic smell such as chlorine or ammonia may be rapidly detected at some distance from its source because of this same phenomenon, which, it must be observed, causes a gas to spread even against gravity. The first quantitative study of diffusion in gases was carried out by *Graham* (1846), who measured the rates at which gases diffuse through a porous material such as earthenware. He established what is known as **Graham's Law of Diffusion**—that *the velocity of diffusion of a gas (i.e. the amount diffusing in a given time) is inversely proportional to the square root of its density*. Thus the velocities of diffusion of oxygen and hydrogen may be compared and it is found that

$$\frac{\text{Velocity of diffusion of O}_2}{\text{Velocity of diffusion of H}_2} = \frac{\sqrt{\text{Density H}_2}}{\sqrt{\text{Density O}_2}} = \frac{\sqrt{1}}{\sqrt{16}},$$

or that hydrogen diffuses about 4 times as fast as oxygen.

A related though not identical phenomenon is that of *effusion*, in which a gas escapes or is forced through a small hole. The same law applies for effusion as for diffusion, *i.e.*

$$\text{Rate of effusion} = \frac{k}{\sqrt{\text{density of gas}}}$$

and the measurement of rates of effusion has been used to determine the vapour density of a gas by comparing it with some standard gas.

The Kinetic Theory of Gases.

The phenomena of diffusion and effusion make a kinetic view of gases a reasonable one, and the other properties of gases are in accord with this theory. According to the kinetic theory, gases are composed of small particles in a constant state of movement. The rapidity of molecular movement is shown by the ease with which gaseous diffusion occurs. The pressure of a gas is due to the constant bombardment of the walls of the containing vessel by the moving molecules, and since the effect of a rise in temperature is an increase in the velocity of the molecules, increase in the temperature of a gas will bring about an increase in pressure. At the absolute zero molecular motion may be supposed to cease altogether, and hence the pressure of a gas would be zero. The

molecules must be assumed to be perfectly elastic particles, since if they were not, momentum would be lost with every collision either with the sides of the vessel or with other molecules, and a decrease in pressure would result. Further, it must be assumed that the actual space occupied by the molecules themselves is very small compared with the total volume occupied by the gas. This is clear from the fact that when liquids vaporise there is a very large increase in volume. Thus water expands to over a thousand times its original volume when it is vaporised, so that the molecules must be very widely separated. The very great compressibility of gases compared with liquids or solids is due to this wide spacing of the molecules. Qualitatively, then, the kinetic theory gives a useful picture of the way in which gases behave and the theory may be made much more informative by putting it on a quantitative basis.

Let u be the speed of the molecules in a gas and let there be n_1 molecules in a cube of sides 1 cm. The motion of the molecules in the cube will be quite at random, but the motion of any particle may be resolved along three axes perpendicular to the faces of the cube. Hence for any one axis it may be assumed that one third of the molecules are moving backwards and forwards along this axis. Hence $n_1/3$ molecules may be considered as moving perpendicular to any particular pair of faces. The number of impacts made on any one face in one second is equal to $un_1/6$ since the molecule after striking has to travel from the original face to the opposite face and back again, a distance of two centimetres, with a velocity u . Hence, since there are $n_1/3$ particles striking this face, the number of impacts per second is $un_1/6$. The change of momentum of a single molecule on impact is from mu to $-mu$, m being the mass of a single molecule—that is to say, a change of $2mu$. Hence the total change of momentum of all the molecules striking one particular face per second is

$$2mu \times \frac{un_1}{6} = \frac{1}{3}mu^2n_1$$

This change of momentum of the molecules must be the force exerted by their bombardment. Hence since the area of the face of the cube is 1 sq. cm., the pressure, *i.e.* force per unit area, is given by :

$$p = \frac{1}{3}mn_1u^2$$

If instead of considering unit volume we consider a volume v containing n molecules, then $n/v = n_1$

and
$$pv = \frac{1}{3}mnu^2n$$

We cannot assume that all the molecules have a velocity u , but this is a certain average value, the "root mean square velocity," round which the velocities of the majority of the molecules lie.

This equation is the quantitative expression of the kinetic theory of gases, and its importance from our point of view lies in its complete consistency with the gas laws.

Thus for any fixed temperature the velocity u of the molecules may be assumed to be constant. For a given mass of gas mn is also constant, and since $pv = \frac{1}{3}mnu^2$, it follows that

$$pv = k$$

for a constant temperature. This agrees with Boyle's Law.

The general Gas Equation follows if it is assumed that the kinetic energy of the gas molecules is proportional to the absolute temperature. On this assumption $\frac{1}{2}mnu^2 = k_1T$ for a given mass, mn , of gas and therefore

$$pv = \frac{1}{3}mnu^2 = \frac{2}{3}k_1T = kT$$

If p is kept constant v is proportional to T —Charles' Law.

Avogadro's hypothesis also follows from the equation of the kinetic theory. For

$$pv = \frac{1}{3}mnu^2n$$

Hence

$$n = \frac{3pv}{mu^2}$$

Therefore when p , v , and T (which is proportional to $\frac{1}{2}mnu^2$) are constant, n will be constant and independent of the nature of the gas. Hence Avogadro's hypothesis that under equal conditions of temperature and pressure equal volumes of all gases contain an equal number of molecules is borne out by the kinetic theory.

Finally it may be shown that Graham's Law of Diffusion also follows from kinetic considerations. It is obvious that the rate of diffusion of a gas depends on the velocity of its molecules.

Now

$$u = \sqrt{\frac{3pv}{nm}}$$

and since $\frac{nm}{v}$ = the density, d , of the gas

$$u = \sqrt{\frac{3p}{d}}$$

or for constant pressures

$$u = k \sqrt{\frac{1}{d}}$$

Hence the velocity of the molecules of a gas and therefore its rate of diffusion varies inversely as the square root of the density.

Example.

Calculate the root mean square velocity of the molecules of oxygen at N.T.P., given that the density of mercury is 13.6 gm. per c.c., $g = 981$ cm. per sec.², and density of oxygen is 1.44 gm. per litre.

$$\begin{aligned} u &= \sqrt{\frac{3p}{d}} = \sqrt{\frac{3 \times 76 \times 13.6 \times 981}{0.00144}} \\ &= 45950 \text{ cm. per sec.} \end{aligned}$$

It will thus be seen that the principal laws governing the behaviour of gases are capable of derivation from the kinetic theory of gases. In considering the quantitative side of the kinetic theory certain assumptions have been made—notably that the gas molecules have no attraction for each other, and that they are negligible in size. Neither of these assumptions is altogether true, and it would therefore be expected that deviations would arise from the gas laws. In fact such deviations do arise and the equation $PV = RT$ would apply only to a ‘perfect gas.’

Deviations from the Gas Laws.

Deviations from Boyle’s Law were investigated by Amagat (1881), who found that the isothermals obtained by plotting values of p_v against p were not straight horizontal lines as would be consistent with Boyle’s Law, but were in every case inclined. The deviations are much more marked at low temperatures and high pressures, as the isothermals in Figs. 18, 19, 20 show.

The next step in the interpretation of the behaviour of gases is to consider the phenomenon of liquefaction. It is well known that increase of pressure (on some gases at room temperature) will bring

about liquefaction, even if the temperature is maintained constant throughout.

Andrews (1863) introduced the conception of *continuity of state* in studying this phenomenon, by which the gaseous and liquid

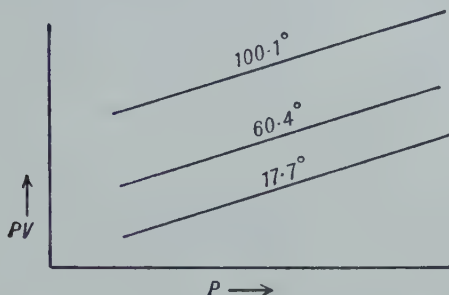


FIG. 18.—ISOTHERMS FOR HYDROGEN.

states are not essentially different, but merely the extremes in a continuous process. He found that for all gases there exists a *critical temperature* above which liquefaction cannot occur, however great the pressure. The *critical pressure* is that

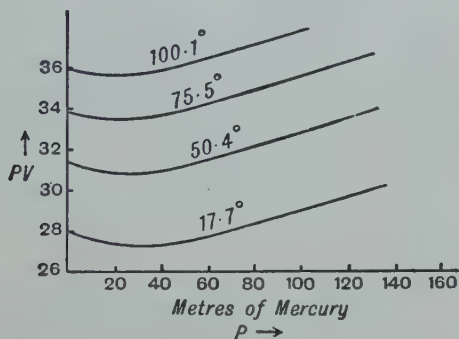


FIG. 19.—ISOTHERMS FOR NITROGEN.

pressure required to bring about liquefaction at the critical temperature, and the *critical volume* is the volume of unit mass of the gas under critical conditions of temperature and pressure. The results of Andrews' experiments are shown in the accompanying

diagram (Fig. 21). It must be noticed that although the lines are isothermals (*i.e.* the temperature remains constant along any one

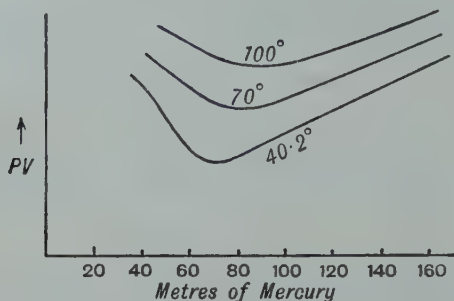


FIG. 20.—ISOTHERMS FOR CARBON DIOXIDE.

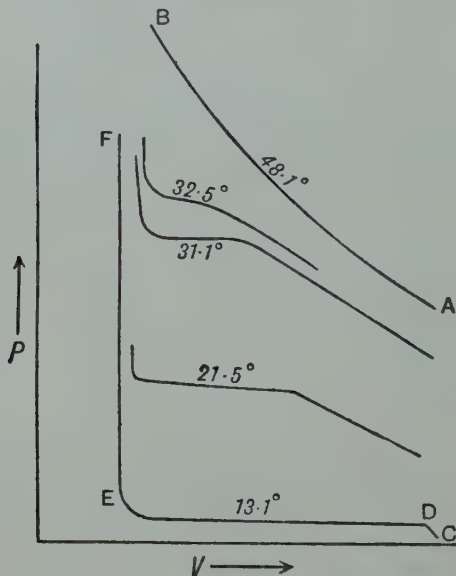


FIG. 21.—ANDREWS' ISOTHERMS FOR CARBON DIOXIDE.

line), it is the pressure that is plotted against the volume, not pv against p as before.

If we consider the isothermal for 48.1°C. , it will be seen that at A

the volume is large and the pressure small. Increase in pressure brings about a decrease in volume, but this decrease is regular and there is no discontinuity in the curve. If we take the isothermal for a lower temperature, however, the behaviour of the gas is quite different. Starting at C , increase in pressure produces a decrease in volume to D in the usual way. At D there is a sharp break, however, and a very large volume change occurs with no increase in pressure. The portion of the curve DE represents the liquefaction of the gas. At E , where liquefaction is complete, another break occurs, and further increase in pressure produces practically no change in volume, *i.e.* EF represents the compression of liquid carbon dioxide. The curves for slightly higher temperatures 21.5°C. and 31.1°C. are similar, though the horizontal portion becomes shorter. With further increase of temperature to 32.5°C. the horizontal portion of the curve disappears, *i.e.* liquefaction does not occur, as the gas is above its critical temperature (31.5°C.). The critical pressure for carbon dioxide is about 73 atmospheres.

Van der Waals' Equation.

Various modifications of the perfect gas equation $PV = RT$ have been suggested to include these deviations of actual gases from the behaviour of a perfect gas. The simplest is that of Van der Waals (1873). It has been said that on the basis of the kinetic theory it would be expected that deviations from the simple equation would occur, since the actual size and the mutual attraction of the molecules had both been neglected. Van der Waals' equation introduces corrections into the perfect gas equation to compensate for these errors. The equation of Van der Waals is obtained by writing $p + a/v^2$ instead of P , and $v - b$ instead of V in the gas equation $PV = RT$, so that we have $(p + a/v^2)(v - b) = RT$, where a and b are constants. The term a/v^2 is introduced to allow for the cohesive forces between the molecules, and its justification is realised by considering the molecules near the surface of the gas which are prevented from exercising their true pressure by the backward pull of the molecules in the gas. Hence the *actual* pressure of a gas is less than the pressure that would be exerted by a perfect gas by a term which depends on the cohesion between molecules. This force may be assumed to be proportional to the square of the density of the gas, or inversely proportional to the

square of the volume. As regards the other term, it is clear that if the volume of the molecules themselves is considered, it must be subtracted from the v of the perfect gas equation, for $v - b$ will be the actual volume in which compression can occur. Hence it is reasonable to write $(p + a/v^2)(v - b) = RT$ instead of $PV = RT$, though the rigid derivation of this formula is much more difficult. It will be seen from the form of Amagat's curves (Fig. 18, 19 and 20) that for gases other than hydrogen, the cohesion between the molecules predominates at low pressures (*i.e.* the value of PV is reduced), while at higher pressures the size of the molecules causes the curves to bend the other way.

If van der Waals' equation is written as

$$v^3 - \left(b + \frac{RT}{p}\right)v^2 + \frac{av}{p} - \frac{ab}{p} = 0$$

it will be seen that it is a cubic equation—that is to say, there should be three values of v for any given values of p and T . This

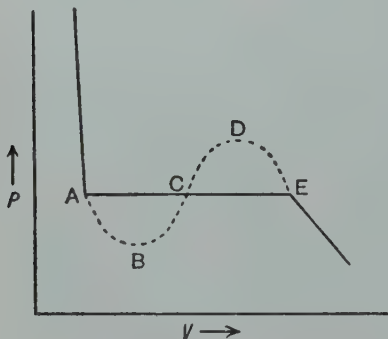


FIG. 22.—THOMSON'S HYPOTHETICAL ISOTHERMAL.

is interesting in view of a suggestion made by James Thomson (1871) following Andrews' work. Thomson suggested that the true form of isothermals was a continuous curve (see Fig. 22), and that Andrews' isothermals represented merely the experimental impossibility of realising the complete continuity between liquid and gas shown by the parts of the curve ABC and CDE . The part ABC represents a super-

heated liquid, and the part CDE represents the compression of a gas into a metastable condition, both of which states are known. The interest of Thomson's hypothetical isothermals lies in the fact that they are precisely the curves demanded by a gas equation of the van der Waals' type. One important result follows from this. For the curve corresponding to the critical temperature, and it will be seen that the three possible values for v have become identical at

the critical volume, temperature and pressure. Thus under these conditions the van der Waals' equation must be of the form

$$(v - v_c)^3 = 0$$

v_c being the critical volume.

$$\text{Hence} \quad v^3 - 3v_c v^2 + 3v_c^2 v - v_c^3 = 0$$

must be identical with

$$v^3 - \left(b + \frac{RT_c}{p_c}\right)v^2 + \frac{av}{p_c} - \frac{ab}{p_c} = 0$$

if T_c and p_c are the values for the critical temperature and pressure. Hence

$$3v_c = b + \frac{RT_c}{p_c}$$

$$3v_c^2 = \frac{a}{p_c}$$

$$v_c^3 = \frac{ab}{p_c}$$

and from this it follows that

$$v_c = 3b$$

$$p_c = \frac{a}{27b^2}$$

$$T_c = \frac{8a}{27Rb}$$

Hence for any gas it is possible to calculate its critical constants by studying its deviations from the gas laws, and the calculated values are in good agreement with those found experimentally.

Corresponding States.

If in van der Waals' gas equation we express p , v , and T as fractions of the critical values, thus :

$$p = \pi p_c, \quad v = \phi v_c, \quad T = \theta T_c$$

we get for the gas equation :

$$\left(\pi p_c + \frac{a}{\phi^2 v_c^2}\right)(\phi v_c - b) = R\theta T_c.$$

And if instead of a and b we write the values obtained above we have :

$$\left(\pi p_c + \frac{3p_c v_c^2}{\phi^2 v_c^2}\right) \left(\phi v_c - \frac{v_c}{3}\right) = \frac{8}{3} \frac{p_c v_c}{T_c} \cdot \theta T_c \left(\text{since } R = \frac{8a}{27bT_c}\right)$$

or $(\pi + 3/\phi^2) (3\phi - 1) = 8\theta.$

This equation is known as the **Reduced Equation of State**, and its importance lies in the fact that it contains no constants characteristic of a particular substance. It will apply to any gas or liquid, and it implies that if two substances are in such a condition that their pressures and volumes are the same fractions of the critical pressures and volumes, then the temperatures will also be the same fractions of the critical temperatures. Substances under these conditions are said to be in **corresponding states**. The physical properties of substances should be compared under conditions in which their states are corresponding.

Limiting Densities and Accurate Molecular Weights.

One important application of the investigation of the deviations of gases from the gas laws is in the accurate determination of the molecular weights of gases. The determination of molecular weights from observations of vapour densities assumes that Avogadro's hypothesis is true. But since various gases show different deviations from Boyle's Law, this assumption is not justified, and hence, although the determination of vapour densities is sufficiently accurate to give *approximate* values for molecular weights (which in most cases are all that are necessary), it will not be accurate enough to give values from which atomic weights may be calculated unless a correction is made for deviations from the gas laws.

If a mass W of a gas occupies a volume v under a pressure p atmospheres at 0°C. , $\frac{W}{pv}$ will be the ordinary density of the gas at N.T.P. $\frac{W}{pv}$ is called the 'density per unit pressure,' and this would be a constant if pv were constant, *i.e.* if Boyle's Law were obeyed. The product pv actually approaches constancy the lower the pressure. Hence the density per unit pressure of a gas should theoretically be measured at zero pressure. Since this cannot be done practically, the value of the density for unit pressure is

determined as the pressure *approaches* zero. This value is called the *limiting density*, and the value of the molecular weight obtained therefrom is accurate. It will be seen that since

$$\text{ordinary density} = \frac{W}{pv}$$

$$\text{and} \quad \text{limiting density} = \frac{W}{p_0 v_0}$$

$$\text{Limiting density} = \text{ordinary density} \times \frac{pv}{p_0 v_0}.$$

One obvious way of obtaining the limiting density is by extrapolation: that is to say, various values of pv are plotted against the pressure, and the value of the product found for $p = 0$. The second method for determining limiting densities applies to those gases which deviate only slightly from Boyle's Law, and where the deviations may be assumed to be proportional to the pressure (see straight line for hydrogen, Fig. 18). The relative deviation of the

gas between zero pressure and pressure p is then $\frac{p_0 v_0 - pv}{pv}$, and

since it is assumed that this is proportional to the pressure, $\frac{p_0 v_0 - pv}{pv} = \lambda p$, where λ is a constant. Since $p = 1$ at 1 atmo-

sphere pressure $p_0 v_0 = p_1 v_1 (1 + \lambda)$, where $p_1 v_1$ is the value of pv when the pressure is one atmosphere, and ordinary density $= \frac{W}{p_1 v_1}$.

$$\text{Limiting density} = \text{ordinary density} \times \frac{p_1 v_1}{p_0 v_0}$$

$$\text{then} \quad \text{Limiting density} = \frac{\text{ordinary density}}{1 + \lambda}$$

λ is called the 'compressibility coefficient' and is determined by taking two observations of pv between zero pressure and 1 atmosphere.

As has been said, the importance of limiting density determinations lies in the very accurate values which they give for the molecular weights of gases, and hence for atomic weights. Thus determinations of the limiting density of nitrous oxide give a value of 1.9623 gm. per litre (the ordinary density is 1.9804 gms. per

litre). This gives a molecular weight of 44.014, and since nitrous oxide is known to be N_2O , the atomic weight of nitrogen is 14.007.

The Liquefaction of Gases.

Although the methods available for the liquefaction of gases are dealt with in textbooks of physics, it will be useful if the general principles employed are summarised, especially in so far as they depend on the kinetic theory of gases.

The first method to be employed for the liquefaction of gases was the application of high pressures, either alone or with the simultaneous use of a freezing mixture. By this means a number of common gases (*e.g.* chlorine, ammonia, and sulphur dioxide) were liquefied early in the nineteenth century. It was found, however, that pressure alone would not suffice for the liquefaction of some gases, such as oxygen, nitrogen, and helium, even when combined with the use of ordinary freezing mixtures. These were therefore called 'permanent' gases. A study of Andrews' isothermals (Fig. 21) explains this behaviour, for it will be seen that above the critical temperature no increase in pressure can possibly bring about liquefaction. As the critical temperature for carbon dioxide is 31.5°C , this gas *can* be liquefied by pressure alone at ordinary temperatures. The same is true of sulphur dioxide (critical temperature 157°C .), ammonia (critical temperature 132°C .), and other gases with high critical temperatures. With oxygen (critical temp. -119°C .), and nitrogen (critical temp. -147°C .), however, pressure cannot produce liquefaction unless they are previously cooled below these temperatures. Once the significance of the critical temperature was understood, the problem of the liquefaction of gases became one of devising methods for intensive cooling as well as applying high pressures. To bring about this cooling three main methods have been employed.

(1) The cooling effect produced by the rapid evaporation of a liquid has been used. This cooling is due to the fact that the latent heat of vaporisation, representing the heat necessary to separate the molecules in changing to the gaseous state is provided by the liquid itself which is thereby cooled. Thus when Pictet first obtained liquid oxygen in 1877 he cooled the gas by the rapid evaporation of liquid carbon dioxide, and later, when Wroblewsky and Olschewsky liquefied the gas in considerable quantities, one of

the methods of cooling they adopted was to surround the gas with liquid ethylene boiling rapidly under reduced pressure.

(2) The second method of cooling that has been used, usually in conjunction with the previous method, is based on the effect produced by causing a gas to expand adiabatically—that is to say, without gain of heat from outside. The external work done by a gas expanding very rapidly against a pressure causes a fall in its temperature. The principle was first used by Cailletet in 1877, and the first practical method of liquefying air devised by Claude depended upon it. The compressed gas was allowed to expand very rapidly, a cooling thus being produced. The cooled gas flowed round the pipes carrying the incoming gas, so that a cumulative cooling effect occurred, leading finally to liquefaction.

(3) When a gas expands there is another kind of cooling effect, called the **Joule-Thomson** effect, which is independent of the external work performed, *i.e.* it would occur if the gas were allowed to expand into a vacuum, in which case no external work would be done. The Joule-Thomson effect is of interest in connection with the kinetic theory, because it arises partly from the *internal* work done in separating the gas molecules against the cohesive force between them, *i.e.* the ' a/v^2 ' term of van der Waals' equation, and partly because $p v$ is not independent of p . The first is always a cooling effect, and the latter is a heating effect above certain temperatures. A perfect gas would show no Joule-Thomson effect. For hydrogen there is at ordinary temperatures a slight *heating* effect on expansion. In this case it is only below -80°C. that the normal effect is observed. This temperature is called the **inversion temperature**, and is in fact the temperature at which the effects due to the attractive forces between molecules and that due to variation of $p v$ with p just balance. The Joule-Thomson effect is used in the Linde process for the manufacture of liquid oxygen, in which air under a pressure of 200 atmospheres is allowed to expand through a small orifice, the cooled gas then cooling the oncoming air.

By the application of these principles all gases have now been liquefied, and temperatures very close to the absolute zero have been obtained by the rapid evaporation of previously liquefied gases. Thus Kamerlingh Onnes produced a temperature of $0.82^{\circ}\text{Absolute}$ by the rapid evaporation of liquid helium. Still lower

temperatures have been reached, but the methods involved are outside the scope of this book.

The Liquid State.

Although the gaseous and liquid states may be considered as continuous if regarded from the point of view of van der Waals' equation, the properties of liquids are very different from those of gases. Whereas the behaviour of gases obeys quite simple laws, with certain deviations already discussed, that of liquids is much more difficult to interpret in simple terms. If we regard liquids from the point of view of the kinetic theory, this difference in behaviour is readily explicable. Whereas the molecules in gases are very far apart, so that the size of the molecules and their mutual attraction (represented by the terms b and $\frac{a}{v^2}$ of van der Waals' equation) are of comparatively small importance, in liquids the molecules are much closer together, and their freedom of movement is therefore more restricted, as is shown by the greater slowness of diffusion in liquids than in gases. Only one or two points connected with the behaviour of liquids will therefore be mentioned here.

Molecular Volumes.

The molecular volume of a substance is the volume in c.c.s occupied by the gram molecular weight, *i.e.* it is the molecular weight divided by the density.

The molecular volume of all gases is, by Avogadro's hypothesis, a constant if measured at N.T.P., since the gram molecular weight of any gas occupies 22.4 litres under those conditions. This regularity led to the investigation of the molecular volumes of liquids and solids. In the case of solids, little information of any value has been obtained, but in that of liquids interesting regularities have been observed, although nothing comparable in value to the results obtained from the study of molecular volumes of gases. The main work on the molecular volumes of liquids was that of *Kopp* (1855 onwards), who measured the densities of the liquids he investigated at their boiling points, since it was obviously necessary to fix some standard condition. Actually a more satisfactory method is to measure the densities at *corresponding tem-*

peratures, *i.e.* at temperatures which are the same fraction of the critical temperatures. Kopp's results were sufficiently accurate, however, to establish the general principle that the molecular volume of a substance is equal to the sum of the atomic volumes of its constituent atoms, together with certain modifications for different types of valency bond. Thus he calculated the atomic volume of carbon as 11, hydrogen as 5.5, oxygen with a double bond as 12.2, oxygen in a hydroxyl group as 7.8, and so on. From the above figures the molecular volume of acetic acid, $\text{CH}_3\cdot\text{C}\begin{smallmatrix} \nearrow \text{O} \\ \searrow \text{OH} \end{smallmatrix}$, should be $(2 \times 11) + (4 \times 5.5) + 12.2 + 7.8$, *i.e.* 64, which agrees well with the observed value of 63.7. Although in some cases, such as this, agreement between experiment and theory is good, the molecular volume is very liable to unexplained deviations due to constitutive influences, and it has been of little use in fixing the structure of compounds whose constitution is doubtful. It is, however, of interest in being an example of a property which is not purely *additive*, like mass, but also partly *constitutive*, *i.e.* structural factors must be taken into account.

Surface Tension.

Measurements of the surface tension of liquids have proved valuable to the chemist in two ways. In the first place, information has been obtained as to the molecular weight of liquids, a quantity which is very difficult to determine. Ramsay and Shields found that the equation

$$\gamma\left(\frac{M}{d}\right)^{\frac{2}{3}} = k(T_c - T - 6)$$

was true for most liquids, where γ is the surface tension, M is the molecular weight, d is the density, T_c is the critical temperature, T is the temperature of observation, and k is a constant (2.12). (This is sometimes referred to as the Ramsay-Shields-Eötvös equation, as its derivation followed some previous work by the last named). In the case of associated liquids (*e.g.* water), the equation is not obeyed unless some multiple of M is used, this multiple being 3 in the case of water, suggesting that liquid water consists of $(\text{H}_2\text{O})_3$ molecules. Thus this relation has led to the detection of association in liquids, and to the approximate determination of the degree to which it occurs. It is not, however, a really reliable or accurate method.

The Parachor.

The other application of surface tension measurements to physico-chemical problems is of much greater importance. Sugden has shown that for any liquid the quantity **molecular volume** $\times$ (**surface tension**)¹ is a constant called the **parachor** of the liquid. The great importance of this quantity is that it really is additive. The parachors of individual atoms and of the various types of link and ring may be determined, and the agreement between the experimental value and the value calculated by the addition of the various factors, atomic and constitutional, for a particular compound, is always good. Hence the use of the parachor is proving of the greatest value for deciding between alternative structures for many compounds.

As an example, benzene, C_6H_6 , has a density of 0.88 gm./ml., its surface tension is 29.2 dynes/cm., and hence its parachor is

$$\frac{\text{Mol. wt.}}{\text{Density}} \times (\text{surface tension})^{\frac{1}{2}} = \frac{78}{0.88} \times 29.2^{\frac{1}{2}} \\ = 206.$$

The parachor values for its constituents are : C = 4.8, H = 17.1, double bond = 23.2 a six-ring = 6.1.

$\therefore$ calculated parachor, **assuming 3 double bonds**

$$= (6 \times 4.8) + (6 \times 17.1) + (3 \times 23.2) + 6.1 = 207.$$

A number of other physical properties of liquids (e.g. refractive index) have been investigated from the physico-chemical point of view, but they have not yielded results important enough to be mentioned here.

The Solid State.

Whereas the molecules of gases and of liquids are in rapid motion, it appears probable that those of solids are stationary, or merely vibrate about a fixed position. Thus crystalline solids are characterised by the fact that they maintain a definite shape, and diffusion in solids does not in general occur at all. The investigation of the positions of atoms in crystals has led to some very important conclusions. It was made possible by the work of Laue and of the Braggs, who found that the planes of atoms in a crystal

were capable of acting as a diffraction grating, not to ordinary light, but to X-rays, which are similar in character, but of much smaller wave-length. Later, the structures were studied not by diffraction but by reflection of light from the crystal planes. By observing the directions taken by the reflected beams of the rays, it was possible to determine the angles of the crystal planes, their distance apart, and also the nature of the atoms of which they are composed. The most striking result of this work from the chemist's point of view has been to elucidate the structures of salts such as sodium chloride. This structure is illustrated in Fig. 23. It will be seen that it is no longer possible to regard sodium chloride as made up of single NaCl molecules.

It consists rather of a *lattice*

of sodium and chlorine *ions*, arranged in such a way that each sodium ion is surrounded by six chloride ions, and each chloride ion by six sodium ions. It should be realised, in connection with the Ionic Theory, that from this information it is clear that such electrolytes are actually completely ionised in the solid state (see p. 178), and that the primary action of the solvent is merely to cause the breaking down of the rigid crystal lattice.

Similar results are obtained with other salts, showing that it is the ion, rather than the individual atom, which is the fundamental unit in the crystal lattice. (For further information the student should read Sir W. H. Bragg and W. L. Bragg *X-Rays and Crystal Structure*).

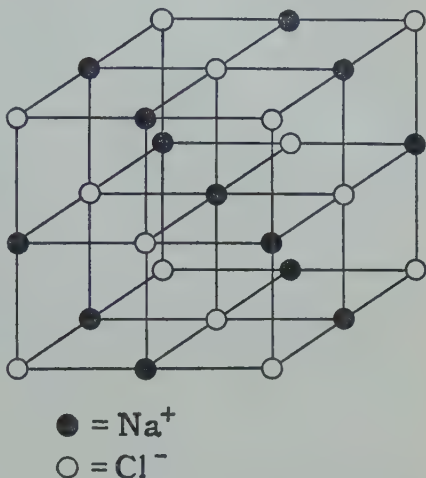


FIG. 23.—STRUCTURE OF SODIUM CHLORIDE.

QUESTIONS ON CHAPTER III.

1. Draw curves illustrating the deviations of gases from Boyle's Law. How are these deviations explained in terms of van der Waals' equation? (O. & C., H.C.)

2. Explain what is meant by the 'gas constant'. If the volume of a gram molecule of gas at N.T.P. is 22.4 litres, calculate the gas constant on the centigrade scale in litre-atmospheres and calories respectively. Calculate the root mean square velocity of carbon dioxide at 23° C. [1 calorie = 4.19×10^7 ergs; density of mercury = 13.6; $g = 981$ cm./sec./sec.; the molecular weight of carbon dioxide = 44.] (Oxf. Prelim.)

3. Indicate the manner in which carbon dioxide deviates from the gas laws. (C.W.B., H.C.)

4. The equation $pV = RT$ represents the behaviour of a perfect gas. Give some account of the deviations from this equation which are observed experimentally. How are these deviations accounted for by van der Waals' equation? (Camb. Schol.)

5. State clearly the assumptions of the kinetic theory of perfect gases, and show that it is a deduction from the theory that the pressure of a gas, $p = \frac{1}{3}dc^2$, where d is the density of the gas and c is the root mean square velocity of the molecule. Show how Graham's Law of Diffusion follows from this relation, and discuss examples of the use of diffusion experiments in chemistry. (Oxf. Schol.)

6. What is meant by the expression 'a perfect gas'? Explain in this connection the following statements:

(a) The pressure exerted by a gas at constant volume varies directly as its absolute temperature.

(b) For the gram-molecular weight $PV = RT$.

(c) The value of R in this expression is approximately 2 cal. per ° C. (Oxf. Prelim.)

CHAPTER IV

SOLUTION

A solution is a homogeneous mixture of two or more substances. As matter is now regarded as discontinuous (molecular) complete homogeneity is impossible, but for true solution we must imagine the particles to be of molecular dimensions and to be uniformly distributed.

It is possible to have suspensions of *insoluble* substances (see Colloids, Chap. X). In some cases these particles are visible to the unaided eye, in others they are smaller and can only be detected by ultramicroscopic methods. Particles forming colloidal suspensions may vary in diameter from 1 to 100 $\mu\mu$ (1 $\mu\mu$ = 1 millionth of a millimetre or 10^{-7} cm.), whereas the size of the molecules of substances dissolved in water vary from 0.1 $\mu\mu$ to 5 $\mu\mu$.

It is convenient to consider solution under the following headings, depending on the normal state of the substances concerned. In general, the substance present in smaller quantity in a solution is called the *solute*; the other is called the *solvent*.

Solids in Liquids.

There is a limit to the amount of a given solid which can dissolve in a fixed quantity of a given liquid.

The solubility is defined as the maximum amount of the solid which can dissolve in 100 grams of the liquid, under given conditions, in the presence of excess of the solid.

The solubility varies considerably with the temperature (see Solubility Curves, Fig. 24), to some extent with the state of subdivision of the solid, and, in some cases, to a slight degree with the pressure.

Saturated solutions of many substances, such as sodium thio-sulphate, on cooling do not always deposit crystals, although the temperature may be very much below that at which a solution of such a strength is in stable equilibrium. Such solutions are said to

be *supersaturated*, and will crystallise immediately on the addition of a small speck of the solid or of an isomorphous substance. In cases where water of crystallisation is taken up the solution may then become completely solid.

Measurement of Solubility of Solids.

Excess of powdered solid is placed in a beaker of water, immersed in a thermostat or constant-temperature bath. The

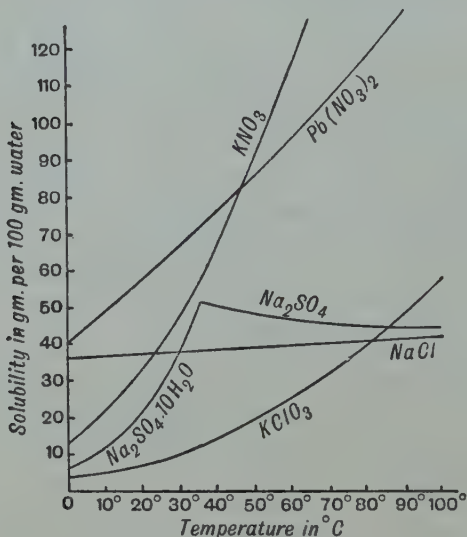


FIG. 24.—SOLUBILITY CURVES.

contents of the beaker are stirred by a mechanical stirrer for several hours.

The composition of the saturated solution may then be determined by various methods.

Method 1.

By means of a pipette (which may have to be warmed to prevent crystals forming in it) fitted with a short rubber extension containing a plug of glass wool to retain solid particles, a quantity of solution is transferred to a weighing bottle.

This bottle may contain some distilled water, so as to avoid crystallisation as the solution cools, and in any case is previously weighed so that the weight of saturated solution can be determined. The contents of the bottle are washed out into a standard flask and made up to a known volume with distilled water.

The strength of this solution, and hence the weight of solid in a known weight of saturated solution, is then determined by a suitable titration.

For example, oxalic acid may be estimated by a standard alkali or by standard potassium permanganate; barium chloride may be estimated gravimetrically by precipitation as sulphate, etc.

Method 2.

A saturated solution is prepared as above, and if there is no convenient titration method possible, then its specific gravity can be measured. By comparing the value obtained with a curve, showing the specific gravities of solutions of the given solid of known strengths, the strength of the saturated solution may be read.

Method 3.

A known weight of saturated solution is carefully evaporated to dryness, on a water-bath, to prevent spitting, and the resulting solid is weighed.

An approximate solubility curve for, say, potassium chlorate, can be obtained quite quickly as follows :

A test tube fitted with a thermometer and stirrer and containing 10 c.c. of distilled water is placed in a boiling tube so as to provide an air jacket.

3 grams of potassium chlorate are added, the apparatus is heated in hot water and then slowly allowed to cool, the solution being constantly stirred.

The temperature at which crystals begin to appear is read. A further 2 c.c. of water are added from a burette, and the temperature at which this diluted solution is saturated is read. The procedure may be repeated until a series of points on the solubility curve have been obtained.

Solution of 'Insoluble' Salts.

Salts which are normally regarded as insoluble have a small, though measurable solubility. This may be calculated from observations of their effect on the electrical conductivity of pure water (see page 199).

Solubility Curves.

Fig. 24 shows some typical examples. It will be noticed that in general the solubility increases with temperature. This is an example of Le Chatelier's Principle,* for most solids dissolve in water with an absorption of heat; hence if heat is applied the system changes so as to oppose the applied change, and more solid dissolves.

The opposite effect is observed in a few cases, such as calcium hydroxide and calcium citrate. When a salt forms several hydrates the curve is discontinuous. For example, the curve for sodium sulphate (see Fig. 24) shows a *transition point* at 32.5°C . Below this temperature crystals of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and above it crystals of Na_2SO_4 are deposited from a saturated solution.

Fractional Crystallisation.

It will be seen from the solubility curves (Fig. 24) that substances may be separated by making use of their different solubilities.

In some cases repeated crystallisation is necessary. Thus if we have a mixture of 50 gm. KNO_3 and 50 gm. KClO_3 one crystallisation from 100 gm. of boiling water will give, on cooling to room temperature, a solid containing 20 gm. KNO_3 and 45 gm. KClO_3 approximately. A further crystallisation from 100 gm. of water will yield about 40 gm. KClO_3 practically free from KNO_3 .

In the separation of salts of the rare-earth elements several thousand such recrystallisations are necessary to effect complete separation.

* If any constraint is applied to a system in equilibrium the equilibrium tends to change in such a way as to annul the effect of the constraint. Many examples of this law occur in Physics.

Liquids in Liquids.

Certain pairs of liquids, such as ethyl alcohol and water, will mix in any proportions, at any rate within wide limits of temperature and pressure.

In other cases, such as ether and water, phenol and water, etc., there are limits to the miscibility. Thus when more than 7% of ether is present in water two liquid layers appear. Moreover if water is added to ether, two liquid layers are formed as soon as about 3% of water is present. The solubility of one liquid in the other and vice versa, and hence the limits of miscibility, will depend on temperature.

In Fig. 25 XY and ZY represent the solubility curves of phenol

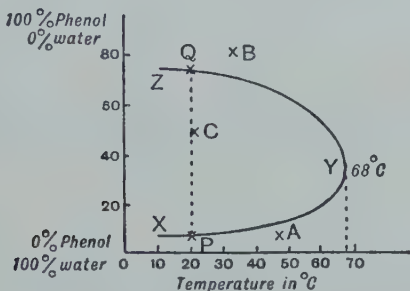


FIG. 25.—MUTUAL SOLUBILITY: PHENOL AND WATER.

in water and water in phenol respectively. The curves meet at Y , and for temperatures above Y these two liquids are completely miscible. The temperature corresponding to Y is called the '**critical solution temperature.**'

For concentrations and temperatures represented by points A and B , phenol will dissolve in water or water in phenol without forming two layers.

If equal quantities of phenol and water are added together at 20°C . as represented by point C , inside the area bounded by the curve, then two layers are formed having compositions represented by the two points P and Q .

On raising the temperature the compositions and densities, and of course other physical properties of the two layers, approach

each other until they are identical at Y , the critical solution temperature.

An interesting example is shown in Fig. 26 for nicotine and

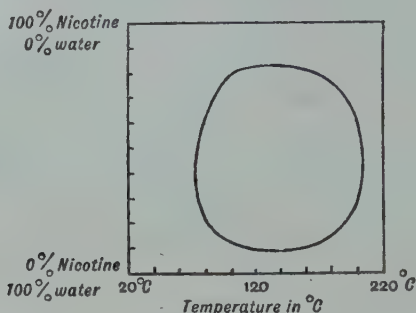


FIG. 26.—MUTUAL SOLUBILITY: NICOTINE AND WATER.

water. The area outside the curve represents conditions of complete miscibility, and a minimum (61°C.) and a maximum (208°C.) critical solution temperature is obtained.

Distillation of Two Liquids.

The principal point of interest in connection with liquid mixtures is concerned with the results of their distillation. Several cases must be distinguished.

Type 1. Non-miscible Liquids.

Each liquid will have its own vapour pressure, which depends on the temperature, but not on the quantity of liquid present.

The vapour pressure of the "mixture" will be the sum of these two vapour pressures and will increase, as they increase, with rising temperature.

When the combined vapour pressure is equal to the atmospheric pressure, the mixture will boil, and this will be at a temperature lower than the boiling point of either constituent. For example, at 98°C. the vapour pressure of aniline is 53 mm. and that of water is 707 mm. Under normal atmospheric pressure (760 mm. = 707 mm. + 53 mm.) a mixture of aniline and water, of any composition, will boil at this temperature.

Steam Distillation.

Using the apparatus shown in Fig. 27, aniline can be separated from non-volatile materials at a temperature below 100°C . by

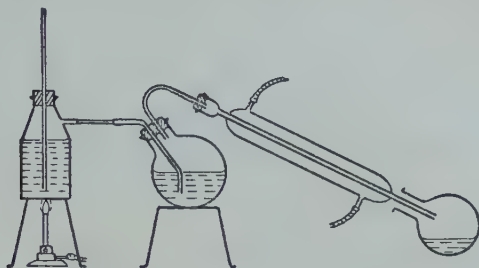


FIG. 27.—DISTILLATION IN STEAM.

passing steam through the mixture. Although the vapour pressure of aniline is small, the weight obtained in the distillate is quite appreciable, for :

$$\frac{\text{Wt. of aniline}}{\text{Wt. of water}} = \frac{\text{Vapour density of aniline} \times \text{volume of aniline vapour}}{\text{Vapour density of water} \times \text{volume of water vapour}}$$

but

$$\begin{aligned} \frac{\text{Volume of aniline vapour}}{\text{Volume of water vapour}} &= \frac{\text{Number of molecules of aniline vapour}}{\text{Number of molecules of water vapour}} \\ &= \frac{\text{Vapour pressure of aniline}}{\text{Vapour pressure of water}} \end{aligned}$$

$$\text{Hence } \frac{\text{Wt. of aniline}}{\text{Wt. of water}} = \frac{\text{Vapour density of aniline}}{\text{Vapour density of water}} \times \frac{\text{Vapour pressure of aniline}}{\text{Vapour pressure of water}}$$

$$= \frac{46.5}{9} \times \frac{53}{707} = \frac{1}{2.5} \text{ approx.}$$

Steam distillation is therefore a practical method which owes its utility to the low molecular weight of water, *i.e.* to the small denominator in the ratio

$$\frac{\text{mol. wt. of substance}}{\text{mol. wt. of water}} \left(= \frac{\text{vap. density of substance}}{\text{vap. density of water}} \right).$$

It will be seen from the above expression that if the molecular weight of one liquid and the ratio of the two vapour pressures are

given, then the molecular weight of the other liquid can be calculated from the composition of the distillate.

Example.

A mixture of ethylene dibromide and water boils at 91° C. under a pressure of 760 mm. The vapour pressure of water at this temperature is 545 mm. and the percentage of ethylene dibromide in the distillate is found to be 80.5% by weight. Calculate the molecular weight of this substance.

The vapour pressure of the ethylene dibromide at 91° C. = $760 - 545 = 215$ mm.

$$\text{Hence } \frac{\text{Wt. of ethylene dibromide}}{\text{Wt. of water}} = \frac{215 \times M}{545 \times 18} = \frac{80.5}{100 - 80.5}$$

where M is the required molecular weight.

$$\therefore M = \frac{80.5}{19.5} \times \frac{545 \times 18}{215} = 188.$$

Type 2. Miscible Liquids.

In this type of mixture the vapour pressure is not equal to the sum of the constituent vapour pressures, and varies with the com-

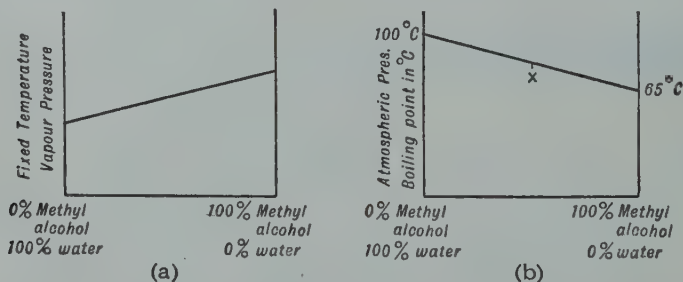


FIG. 28.

position of the mixture. In the case of methyl alcohol and water this is a straight-line variation (see Fig. 28), the vapour pressure of the mixture being equal to the sum of the partial pressures of the constituents. In other cases, the curves showing the relation between vapour pressure and composition exhibit maxima and minima.

Case I.

For methyl alcohol and water Fig. 28(a) shows the variation of

vapour pressure with the composition of the mixture and Fig. 28(b) shows the temperatures at which different mixtures boil. In the latter, of course, we must assume constant pressure (atmospheric). Similar curves are obtained for mixtures of aniline and ether.

A mixture of equal parts of methyl alcohol and water will boil at 83°C . as represented by the point X in Fig. 28 (b). The vapour will, however, contain a higher proportion than the liquid of the lower-boiling-point constituent, methyl alcohol.

The remaining liquid will thus contain less than 50% alcohol and, on applying more heat, its boiling point will be higher than 83°C . Similarly if the vapour is condensed and again heated, the boiling point will be lower than 83°C . By a series of distillations practically complete separation of the two constituents is obtained.

In practice this operation is performed in a ***fractionating column*** in which each constriction, or arrest point, contains liquid in contact at its boiling point with vapour richer than the liquid in the lower-boiling-point constituent. A series of ordinary distillations therefore takes place at each constriction at temperatures falling as the column is ascended. One type of fractionating column is illustrated in Fig. 29.

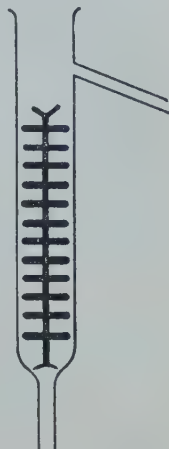


FIG. 29.—FRACTIONATING COLUMN.

Case 2.

The vapour-pressure/composition curve for a mixture of ethyl

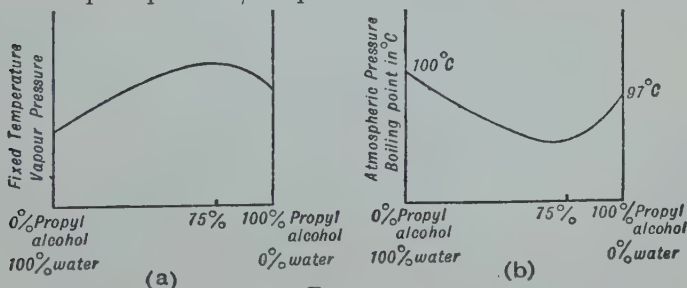


FIG. 30.

alcohol and water shows a maximum vapour pressure when 96% alcohol and 4% water are present in the liquid. Similarly a

maximum vapour pressure is obtained when a mixture of propyl alcohol and water contains 75% of the former. Fig. 30(a) and (b) shows the vapour-pressure curve and the boiling-point curve, respectively, for mixtures of propyl alcohol and water.

If such a mixture is heated, the mixture having this maximum vapour pressure will boil off first, leaving the liquid increasingly rich in that liquid which is in excess of the maximum vapour-pressure mixture.

Case 3.

Similar curves are obtained for mixtures of hydrochloric acid and water, sulphuric acid and water, and nitric acid and water, except that in these cases the vapour-pressure curves show a minimum and the boiling-point curves a maximum.

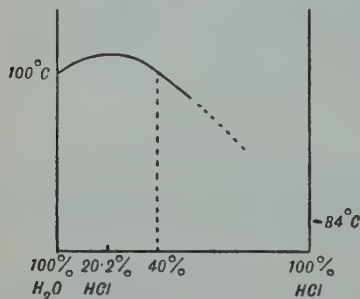


FIG. 31.—BOILING-POINT CURVE: OF HYDROGEN CHLORIDE AND WATER.

Fig. 31 shows the boiling-point curve for hydrogen chloride and water.

A solution containing, say, 40% HCl will boil at about 90° C., giving off mostly HCl until the remaining solution contains only 20% HCl, when it will boil unchanged at 110° C. A weak solution, on the other hand, will give off water when boiled, thus becoming stronger until the composition reaches 20% HCl.

These '**constant-boiling-point mixtures**' (sometimes called **azeotropic** mixtures), whether with definite maximum or minimum boiling points, and in which the composition of liquid and distillate is the same, bear some resemblance to chemical compounds. This is especially true if, as in some cases, the composition is such that it may be expressed as a simple molecular formula. However, if the pressure is changed, not only is the boiling point changed (this

For hydrogen chloride and water the minimum vapour pressure mixture at normal atmospheric pressure contains 20.2% hydrogen chloride and it boils at 110° C. The corresponding figures for sulphuric acid and water are 98.7%, 338° C., and for nitric acid and water 68%, 120° C.

is true for compounds), but the composition of the mixture also changes. It is obvious that such mixtures (cases 2 and 3) cannot be separated by fractional distillation. The 4% water in a mixture of ethyl alcohol and water can only be removed by distilling the alcohol over quicklime.

In Figs. 28(b) and 30(b) curves were given to show the variation of boiling point with composition for mixtures of methyl alcohol and water, and propyl alcohol and water, respectively. Since at any given boiling point, except that of the constant-boiling-point mixture, the composition of the vapour differs from that of the liquid, these are approximate curves. Strictly each curve consists of two parts: one showing the composition of the liquid, and

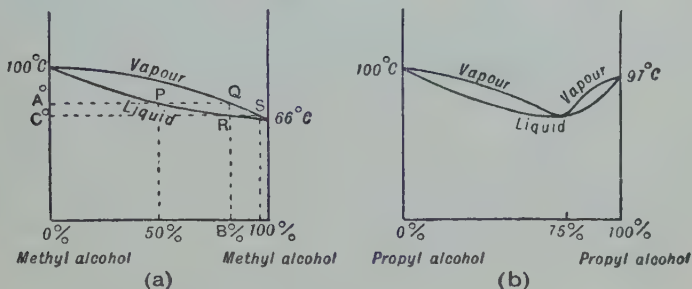


FIG. 32.

the other that of the vapour in equilibrium with it at each boiling point. Such double curves for methyl alcohol and water, and for propyl alcohol and water are shown in Fig. 32. A 50% solution of methyl alcohol and water will boil at P ($A^\circ \text{C.}$), and the composition of the vapour will be represented by Q ($B\%$ methyl alcohol). If this vapour is condensed and the liquid so obtained is reheated, then it will boil at R ($C^\circ \text{C.}$), and the composition of the vapour in equilibrium with this liquid will be represented by S . The mixture can thus be completely separated into its pure components by fractionation.

On the other hand, a mixture of type Fig. 32(b) can be fractionated to give the constant-boiling-point mixture together with one or other of the pure components, depending on whether the original mixture contains more or less than 75% propyl alcohol.

Type 3. Partially Miscible Liquids.

The vapour pressure, in this case, will be the sum of those of the two immiscible layers (see Type 1) and independent of the quantities of the two substances. In each layer the presence of one constituent may either raise or lower the vapour pressure of the other, and the problem of the results of distillation must be left to a more advanced treatise.

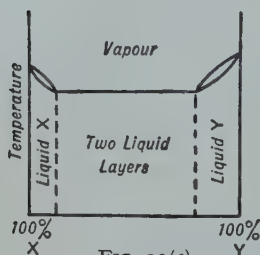


FIG. 32(c).

A typical Temperature-Composition diagram for two partially miscible liquids is given in Fig. 32(c).

Solubility in Two Liquids.

When a third substance is added to two non-miscible liquids in both of which it is soluble, it will distribute itself between them according to the **Partition Law**. If neither solution has reached saturation, then it is found that the concentration of substance in one liquid—say C_A grams per c.c.—bears a constant ratio to its concentration in the other, say C_B grams per c.c.

$$\frac{C_A}{C_B} = \text{a constant, the Partition Coefficient or Distribution Coefficient.}$$

This coefficient varies, of course, with different substances, but with given substances, at constant temperature, it is independent of the total quantities used.

For example, if succinic acid is shaken with ether and water :

$$\frac{\text{Conc. succinic acid in ether}}{\text{Conc. succinic acid in water}} = \frac{1}{5}$$

Similarly iodine distributes itself between carbon disulphide and water thus :

$$\frac{\text{Conc. iodine in carbon disulphide}}{\text{Conc. iodine in water}} = \frac{420}{1}.$$

Experimental Determination of the Partition Coefficient of Iodine between Benzene and Water.

About 200 c.c. of water and 50 c.c. of benzene are placed in a stoppered bottle immersed in a constant-temperature bath. About 1 gm. of iodine is added and the mixture well shaken, and then allowed to separate into two layers. Portions of 20 c.c. from the water layer and 5 c.c. from the benzene layer are pipetted off and their iodine content is determined by titration with a standard solution of sodium thiosulphate. Another gram of iodine is now added to the mixture and the strengths of the solutions are again determined. This process is repeated and the results are tabulated to show that the ratio of the concentrations of iodine in the two layers remains constant.

The partition of succinic acid between ether and water may be similarly examined standard baryta being used for estimating the concentrations of the acid.

Abnormal Results.

In several cases this simple distribution law does not give a constant value.

For example, for acetic acid in benzene and water it is found that :

$$\frac{\text{Conc. of acetic in benzene}}{(\text{Conc. of acetic in water})^2} = \text{a constant} = K$$

or $\frac{\sqrt{\text{Conc. of acetic in benzene}}}{\text{Conc. of acetic in water}} = \text{a constant (actually } \sqrt{K} \text{)}.$

By the Law of Mass Action (see page 137) this can be explained as due to the fact that acetic acid is 'associated' into double molecules $(\text{CH}_3\cdot\text{COOH})_2$ when in solution in benzene. It might be equally well explained as due to the fact that the acetic acid molecule is split into two parts when in water. Similarly it is found that benzoic acid is associated in benzene, and that acetic acid is associated in other solvents such as carbon tetrachloride.

Confirmatory evidence is obtained from molecular-weight determinations by such methods as the elevation of the boiling point of the solvent (see page 123).

The simple partition law, then, applies only if the substance

concerned has the same molecular complexity in the two solvents.

Another interesting experiment on the distribution law is to prove the probable existence of KI_3 molecules in a solution of iodine in potassium iodide. When such a solution is shaken up with chloroform or carbon disulphide, titration with 'hypo' will give the concentration of iodine in the chloroform layer and from a previous determination of the partition coefficient of iodine between chloroform and water the concentration of *free* iodine in the latter can be calculated. A separate titration of the aqueous layer will give the total iodine (the free iodine + that combined with potassium iodide).

The equilibrium $KI + I_2 \rightleftharpoons KI_3$ can thus be investigated. Important examples on the application of the partition law will be found in connection with the solubility of gases (see page 90).

Extraction with Ether.

Many substances, especially organic compounds, are more soluble in ether or benzene than in water, and this fact provides a basis for their separation from impurities such as salts which are insoluble in such solvents. After extraction the volatile ether or benzene is easily removed.

For example, aniline may be prepared from nitrobenzene by reduction with tin and hydrochloric acid. The crude product is made strongly alkaline with sodium hydroxide, and the aniline, set free as an oil, is 'distilled in steam', salts such as sodium stannate and sodium chloride being left behind. Although aniline is only soluble to the extent of 3% in cold water 'extraction with ether' is then carried out to give almost complete separation of the aniline.

It can be shown that in such extractions it is more profitable to use the given supply of, say, ether, in separate fractions than in one complete dose.

Suppose that 100 c.c. of ether are available, that the substance is originally present in 100 c.c. of water and that the partition coefficient

$$\frac{\text{Conc. of substance in ether}}{\text{Conc. of substance in water}} = \frac{5}{1}.$$

If 50 c.c. of ether are added, then the substance will distribute itself so that W_e gm. and W_w gm. of substance are in the ether and water layers where :

$$\frac{W_e}{50} / \frac{W_w}{100} = \frac{5}{1} \text{ or } \frac{W_e}{W_w} = \frac{5}{2} \text{ or } \frac{W_e}{W_e + W_w} = \frac{5}{7}.$$

i.e. $\frac{5}{7}$ of substance will have been extracted and $\frac{2}{7}$ will remain. On adding the other 50 c.c. of ether to this remainder, a further $\frac{5}{7}$ of $\frac{2}{7}$ will be extracted and $\frac{2}{7}$ of the $\frac{2}{7}$ will remain.

Hence amount extracted $= \frac{5}{7} + \left(\frac{5}{7} \times \frac{2}{7} \right) = \frac{45}{49}$ of amount originally present.

If the whole 100 c.c. of ether had been added at once, then

$$\frac{W_e}{100} / \frac{W_w}{100} = \frac{5}{1} \text{ or } \frac{W_e}{W_w} = \frac{5}{1} \text{ or } \frac{W_e}{W_e + W_w} = \frac{5}{6}.$$

Hence amount extracted equals $\frac{5}{6}$ of amount originally present. This is less than $\frac{45}{49}$.

It would be still more satisfactory to use the same quantity of ether in smaller portions, e.g. four of 25 c.c. each.

Gases in Gases.

One gas is completely miscible with another in all proportions, and the physical properties of the mixture will be intermediate between those of the constituents and in proportion to the amounts of each gas present.

Dalton's Law of Partial Pressures.

The total pressure of a mixture of gases is the sum of the pressures which would be exerted by each of the components if it alone occupied the volume of the mixture.

Thus dry air contains approximately 4 volumes of nitrogen to 1 volume of oxygen, and at atmospheric pressure the partial pressures of these two gases will be $\frac{4}{5}$ atmosphere and $\frac{1}{5}$ atmosphere.

In collecting and measuring gases over water, when the water levels have been adjusted, the pressures of the dry gas and the water vapour together equal that of the atmosphere. The satur-

ated water vapour pressure depends on the temperature, and its value can be obtained from tables. On subtracting this from the atmospheric pressure, that of the dry gas is obtained.

Gases in Liquids.

Various definitions of the solubility of a gas are in use, and much confusion results.

The simplest course is to define the solubility as ***the volume of gas in c.c. measured under the given conditions of temperature and pressure which will saturate 1 c.c. of the liquid, under these conditions.***

The volume, *when reduced to N.T.P.*, of the gas which will saturate 1 c.c. of the liquid under given conditions of temperature and pressure is then called the ***absorption coefficient.***

The above definition of *solubility* is, however, sometimes called the *absorption coefficient* and the solubility is then defined as the *mass* of gas which will saturate 1 c.c. of the liquid under the given conditions. Care should be taken, in reading tables of solubilities, to discover exactly what the figures mean.

The solubility of all gases will diminish with rise of temperature. Thus water will dissolve about three times as much oxygen and about seven times as much ammonia at 0° C. as at 100° C.

Henry's Law (1803).

The effect of pressure on solubility of gases is summed up in Henry's Law which states that ***The mass of gas dissolved at constant temperature by a given volume of liquid is proportional to the pressure of the gas.***

It should be noticed that if the pressure is doubled, the *mass* of gas will be doubled, but that since volume is inversely proportional to pressure, the *volume* of gas as measured under the doubled pressure will be the same as the original volume. In other words, the solubility as defined at the beginning of this section will be independent of the pressure.

Henry's Law and Partition Coefficient.

Henry's Law may be regarded as an application of the principle of the Partition Coefficient (see page 86) for :

$$\frac{\text{Conc. of gas in gaseous layer}}{\text{Conc. of gas in solution}} = \text{a constant.}$$

Now, concentration of gas in gaseous layer is proportional to its pressure, and concentration of gas in solution is proportional to its weight per c.c. of solution

$$\text{Hence } \frac{\text{Pressure of gas}}{\text{Wt. dissolved per c.c.}} = \text{a constant}$$

Moreover, if the gas were associated into double molecules in solution we should have

$$\frac{(\text{Pressure of gas})^2}{\text{Wt. dissolved per c.c.}} = \text{a constant}$$

and if it were completely dissociated into two parts we should have

$$\frac{\sqrt{\text{Pressure}}}{\text{Wt. dissolved per c.c.}} = \text{a constant.}$$

Exceptions to Henry's Law.

This law is not true for the very soluble gases such as hydrogen chloride or ammonia, and is true for carbon dioxide only at fairly low pressures.

These deviations are sometimes regarded as proof of the formation of a chemical compound between the gas and the solvent; but this is not a sound argument.

Provided that the concentration of gas in the solvent is taken as the total amount of gas (both free and combined molecules), then :

$$\frac{\text{Pressure of gas}}{\text{Wt. dissolved per c.c.}}$$

is still a constant, although the actual value of the constant is not the same as it would be if no chemical combination had occurred. This is a direct deduction from the Law of Mass Action.

If, however, the gas is associated or if ionisation occurs in the solution, Henry's Law will not be applicable.

Moreover, under high pressures further discrepancies occur, for Henry's Law, like other gas laws, is strictly true only for perfect gases and dilute solutions.

Measurement of Solubility of Gases.

Sparingly Soluble Gases.

The apparatus shown in Fig. 33 is used, and consists of two gas pipettes, *A* and *B*, joined through two three-way taps by a piece of flexible tubing. *A* and the flexible tube are filled with gas at atmospheric pressure, and the volume of gas in *A* is read with the mercury levels adjusted to be the same. *B* is filled with gas-free

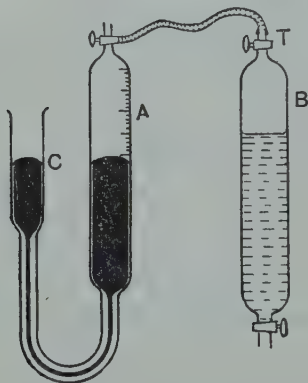


FIG. 33.—APPARATUS FOR MEASURING SOLUBILITY OF GASES.

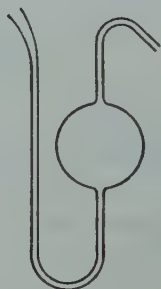


FIG. 34.

distilled water of volume V and, with the taps adjusted to connect *A* and *B*, some water is run out from *B* and its volume v is measured. At the same time the tube *C* is raised to drive some of the gas into *B*. The tap *T* is now shut and the gas and water in *B* are shaken. When no more gas will dissolve, the mercury levels are again adjusted and the volume of gas remaining in *A* is measured. A volume v of gas at atmospheric pressure also remains in *B*. Hence the volume of gas which has dissolved in a volume $(V - v)$ of water is known. For accurate results the pipettes should be kept in a thermostat.

Very Soluble Gases.

A saturated solution of the gas is prepared under the given conditions of temperature and pressure by bubbling a slow stream of gas through the liquid. The concentration of the solution may

then be determined by some suitable titration method. Thus ammonia may be neutralised by excess of standard acid and the unchanged acid back titrated with standard alkali. Similar titration methods may be used for hydrogen chloride, sulphur dioxide, and chlorine. Even the much less soluble carbon dioxide may be estimated by standard baryta.

The apparatus, Fig. 34, of known weight, is often used. The glass bulb of approximately 50 c.c. capacity is about half filled with liquid. The apparatus is placed in a thermostat, and gas is bubbled through the liquid until saturation point is obtained. The apparatus is sealed up, by drawing out the ends, and the whole is weighed to give the weight of saturated solution.

It is then broken under a suitable reagent and the amount of gas determined by titration as above.

The Solution of a Mixture of Gases in a Liquid.

By the application of Dalton's Law of Partial Pressures (see page 89) and of Henry's Law (see page 90) the composition of air dissolved in water can be calculated as follows.

The solubility of oxygen in water at 15° C. and 760 mm. pressure is about twice (by volume) that of nitrogen under similar conditions.

Air contains approximately 80% nitrogen and 20% oxygen by volume. Hence at atmospheric pressure the partial pressure of the nitrogen is $\frac{4}{5} \times 760$ mm. and of the oxygen $\frac{1}{5} \times 760$ mm.

The volume of each gas dissolved will be proportional to its solubility and to its partial pressure.

$$\text{Hence } \frac{\text{Volume of oxygen in dissolved air}}{\text{Volume of nitrogen in dissolved air}} = \frac{2 \times \frac{1}{5}}{1 \times \frac{4}{5}} = \frac{1}{2}$$

Thus, using these approximate figures, the percentage of oxygen in dissolved air, by volume, is $33\frac{1}{3}\%$.

Gases in Solids.

(1) The gas may form a chemical compound with the solid, and in this case when equilibrium is reached the pressure of the gas has a constant value depending on the temperature only, and not on the quantities of substances present. This will be true unless the solid solvent is saturated—that is, completely converted into the new compound. For example, the 'dissociation pressure' of carbon

dioxide in contact with calcium oxide and calcium carbonate (see also page 96) depends only on the temperature.

(2) If the gas dissolves physically, the ordinary partition law should apply, thus:

$$\frac{\text{Pressure of gas}}{\text{Conc. in solid}} = \frac{P}{C} = \text{constant.}$$

or $\frac{(P)^n}{C} = \text{constant}$ if the molecules of the gas are associated and

$\frac{\sqrt[n]{P}}{C} = \text{constant}$ if they are dissociated when in the solid.

(3) In many cases the equation $\frac{\sqrt[n]{P}}{C}$ is found to fit the facts when n is not an integer, but is always greater than unity. This would imply that the gas, especially if normally monatomic, was present in the solid as fractions of atoms.

The phenomenon is then regarded as '*adsorption*,' the gaseous molecules being concentrated, at any rate at first, in the surface layer of the solid. This is consistent with the fact that the solution of the gas is very rapid, although a slow diffusion of the gas into the interior may take place later. It should be noticed that the Law of Mass Action from which Henry's Law equation is deduced would only apply to cases of homogeneous distribution of the gas throughout the mass of the solid. The catalytic effect of such surfaces (see page 235) is therefore due partly to this concentration of the gas and increase in its active mass, partly to the activation (see page 236) effect of the surface, and partly to the fact that these molecules of gas in the surface are rather specially orientated.

Solids in Solids.

It is well known that metals when left in contact for very considerable periods do very slowly diffuse one into the other.

When two isomorphous salts in solution crystallise out mixed crystals are often obtained. Any one crystal contains both substances and is in fact a homogeneous solid solution. The problem of the solution of solids in solids is especially important in the case of metals as throwing light on the nature and behaviour of alloys.

As in the case of 'liquids in liquids' three types are distinguishable.

(a) Miscible Solids.

These give genuine solid solutions, as in the case of mixed crystals, or isomorphous mixtures, obtained with salts such as the alums. For metals a simple example is shown in Fig. 35(a), which gives the melting-point curve for mixtures of silver and gold. Copper and nickel give a similar curve.

As in the case of boiling point-composition diagrams (see page 85), this curve strictly should consist of two parts, a liquidus and a solidus curve. These show the compositions of the liquid and solid phases in equilibrium at each temperature, and are in fact the freezing-point and melting-point curves respectively.

It should be clearly understood that as the solid which separates out, on cooling such mixtures, is never pure solvent, the ordinary lowering of the freezing point law (see page 128) does not apply.

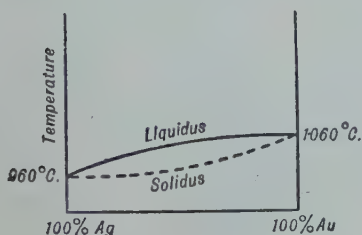


FIG. 35(a).

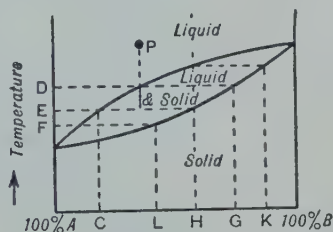


FIG. 35(b).

In Fig. 35(b) a liquid mixture of composition and temperature represented by the point *P* will, when cooled, begin to deposit solid solution of composition *G* at temperature *D*.

If it is further cooled to temperature *E*, the solid deposited will have composition *H*, and the liquid will have composition *C*.

If the solid of composition *H* is remelted and again allowed to cool the solid solution which begins to separate will have composition *K*. It will be much richer in substance *B* than the original mixture. Similarly, the liquid of composition *C* can be cooled below temperature *E* to *F*, giving a solid of composition *L*.

Repetition of these processes—***fractional crystallisation***—can give complete separation of *A* and *B*.

In most cases of this type the freezing point-composition curve

does not approximate to a straight line. Some pairs of substances give maximum melting point solid solutions, others give minimum melting point solid solutions. A good example of the latter is fusion mixture, which melts at more than $100^{\circ}\text{C}.$ below the melting points of its constituents, sodium and potassium carbonates.

(b) *Non-miscible Solids.*

For pairs of metals and other solids which come under this heading one solid only will in general crystallise out on cooling the molten mixture. Thus the ordinary lowering of the freezing point

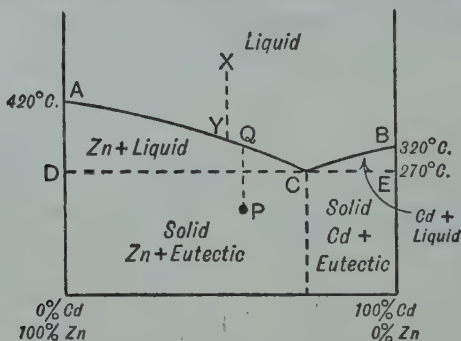


FIG. 36.

law (see page 128) will apply. A small amount of one will lower the freezing point of the other by an amount proportional to the quantity present, and vice versa. Thus in Fig. 36 for zinc and cadmium AC represents the effect on the freezing point of zinc produced by the addition of cadmium and BC that of adding zinc to cadmium. The point X represents a 50% mixture at $450^{\circ}\text{C}.$ On cooling, this deposits pure zinc at Y ; the liquid therefore is richer in cadmium and freezes at a lower temperature. At C zinc and cadmium separate out together, the composition of the liquid being the same as that of the solid.

This solid is called a **eutectic mixture** and the point C a **eutectic point**. ACB is the liquidus and DCE the solidus curve.

If a solid mixture of composition and temperature represented

by point *P* is heated liquid will form when the temperature reaches *D*, and it will have the composition of the eutectic. This will continue until all the cadmium has melted. Further rise of temperature causes the melting of zinc (which is present in excess of that required in the molten eutectic), and this melting is complete at *Q*. Before such a point is reached, in fact at any point in the area *ACD* (or *BCE*), we have a pasty mixture of one solid metal and liquid.

As in the case of a constant-boiling-point mixture, the eutectic is not a chemical compound for its melting point *and composition* will vary with the pressure.

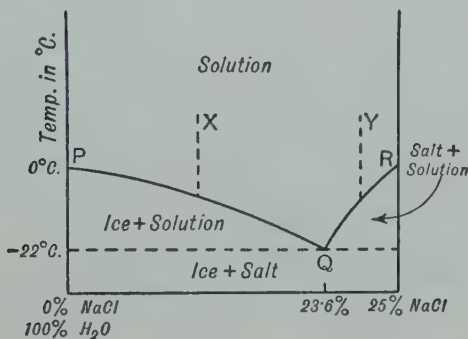


FIG. 37.

Moreover, using a microscope, the crystals of the two solids may be seen separately, and so a true solid solution is not present. Tin and lead give a somewhat similar pair of curves. A wide 'pasty' area between the liquidus and solidus curves explains the useful property of the tin-lead alloy solder.

Similar effects are found when solutions of various salts in water are cooled. For example, in Fig. 37 *PQ* represents the effect on the freezing point of water of adding varying amounts of common salt, and *RQ* represents the solubility curve of common salt.

A weak solution of salt represented by the point *X* will, after cooling until the curve *PQ* is reached, freeze and deposit pure ice. The remaining solution will be stronger and therefore have a lower

freezing point. Similarly a strong solution represented by the point *Y* will, on cooling, deposit pure salt (actually a hydrate—see below).

In either case a solution containing 23.6 gm. sodium chloride in 100 gm. solution will eventually remain, and this will 'freeze' as a whole at -22°C .

A eutectic mixture in which one of the constituents is ice is called a **cryohydrate**—the point *Q* is the **cryohydric point**.

The solubility curve for sodium chloride is given, in the figure, only from the cryohydric point up to 0°C . Between these temperatures the hydrate $\text{NaCl}\cdot 2\text{H}_2\text{O}$ crystallises out. Above 0°C , NaCl crystallises out according to the ordinarily familiar solubility curve.

These simple eutectic diagrams are sometimes complicated by the formation of a definite chemical compound, which will have its own fixed melting point. Fig. 38 shows such a diagram for the metals magnesium and zinc. The melting point of the compound MgZn_2 is represented by the point *Z*. The point *X* represents a eutectic mixture of magnesium and compound and *Y* the eutectic mixture of zinc and the compound.

Melting-point figures of this type, produced from experimental observations, are valuable in showing the existence of solid solutions, eutectics, and compounds.

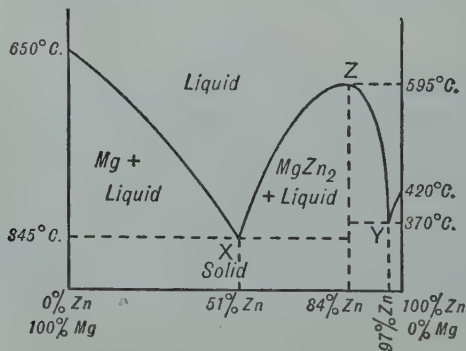


FIG. 38.

(c) *Partially Miscible Solids.*

Solid solutions, eutectic mixtures, and chemical compounds may be formed between the same substances at various concentrations.

The diagrams, therefore, become rather complicated, especially when drawn, as all the above should be drawn, in three dimensions since, strictly, variations in pressure should be shown on a third axis. The diagrams shown in this book refer only to results under one fixed pressure.

In the case of iron and carbon, *martensite* is a solid solution of carbon in iron, *pearlite* is a eutectoid mixture, and *cementite* is the compound Fe_3C . When it is realised that there are also three allotropic varieties of iron, the complicated behaviour of iron and steel is understandable.

The Phase Rule.

Before the Phase Rule is stated three conceptions used must be clearly understood.

(1) Phase.

Phases are the homogeneous parts of a system. They are physically distinct, that is, there is a boundary between them at which a marked change in physical properties occurs. These phases are mechanically separable.

Thus unless a solid solution is present the number of solid phases will be the same as the number of solids present. Similarly several liquids, except where immiscibility causes a double layer, will constitute a single phase.

A mixture of any number of gases is regarded as constituting only one phase.

(2) Component.

We are not concerned so much with the actual components as with their number. The number of components is defined as the least number of constituent substances in terms of which the composition of each and all of the phases may be defined.

Thus in the system CaCO_3 , CaO , CO_2 the *constituents* may be regarded as these three substances.

If any two of these are chosen the composition of each phase may be defined.

Thus

CaCO_3 phase may be expressed as x gm. CaCO_3

CaO " " " y gm. CaCO_3 — $\frac{44}{100} y$ gm. CO_2

CO_2 " " " z gm. CO_2

Again

CaCO₃ phase may be expressed as a gm. CaO + $\frac{44}{56}a$ gm. CO₂

CaO " " " b gm. CaO

CO₂ " " " c gm. CO₂

or again

CaCO₃ phase may be expressed as p gm. CaCO₃

CaO " " " q gm. CaO

CO₂ " " " r gm. CaCO₃ - $\frac{56}{100}r$ gm. CaO

Hence the composition of each phase may be expressed in terms of two constituents, CaCO₃ and CO₂, CaO and CO₂, or CaCO₃ and CaO, but no less. Two is therefore the number of *components*.

(3) *Degrees of Freedom.*

The number of degrees of freedom is the number of variable factors, such as temperature, pressure, or concentration of reacting substances which must be arbitrarily fixed in order that the equilibrium shall be fixed.

For example, a system consisting of a liquid and its vapour is in equilibrium if the temperature is arbitrarily fixed for it then has a fixed vapour pressure. Such a system has therefore one degree of freedom.

The Phase Rule was stated by Willard Gibbs in 1875, as follows :

P = number of phases

F = number of degrees of freedom

C = number of components

then for a system in equilibrium

$$P + F = C + 2.$$

Illustrations.

(1) *A gas.*

$$P = 1; C = 1$$

$$\therefore F = 1 + 2 - 1 = 2.$$

This is clearly true, for the pressure and temperature of a given mass of gas must be independently fixed before its volume is thereby fixed.

(2) *Ice and Water.*

$P = 2$; $C = 1$ (viz. H_2O or Oxygen, or Hydrogen)

$$\therefore F = 1 + 2 - 2 = 1.$$

If the pressure is fixed, then there is only one temperature at which ice and water can exist in equilibrium together.

(3) *Ice, Water, and Water Vapour.*

In this case there is an extra phase (water vapour) compared with (2), and therefore, there are no degrees of freedom. No factor can be arbitrarily fixed, and ice, water, and its vapour can only exist together at $0.0076^\circ C.$ and under a pressure of 4.6 mm. This is illustrated in Fig. 39.

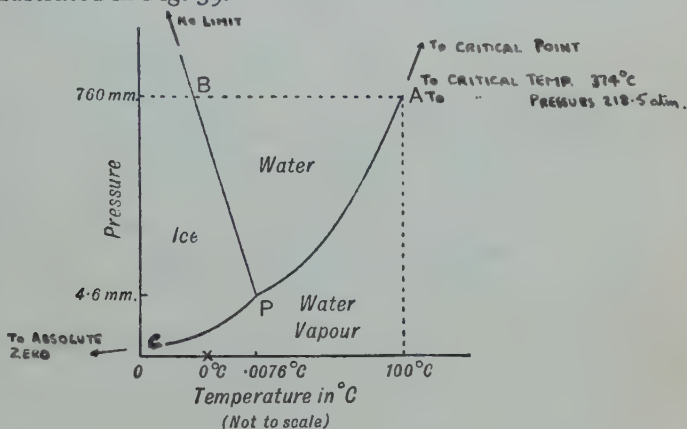


FIG. 39.—TRIPLE POINT FOR WATER.

AP—The steam line shows the conditions under which water and water vapour can exist together in equilibrium. This is a system with one degree of freedom—that is, for each temperature there is a fixed aqueous vapour pressure.

BP—The ice line shows the effect of pressure on the melting point of ice—that is, the condition of equilibrium between ice and water.

The third line at *P*, the hoar-frost line, shows the vapour pressure of solid ice, in the absence of water, at varying temperatures.

The point *P* shows the only conditions under which ice, water,

and vapour can co-exist in equilibrium, and is known as the **Triple Point**.

It will be noticed that a point on such a diagram represents no degrees of freedom, a line represents one, and an area two.

In such a system as that illustrated in Fig. 39 (and in Fig. 40(a)), vapour if cooled, the pressure being below that of the triple point, will condense to solid without passing through the liquid state.

The converse, **sublimation**, can also occur, especially with substances such as iodine, whose triple point is 114°C .

The use of carbon dioxide in refrigerators depends on the fact that, at room temperature, it **sublimes** unless the pressure is above that of the triple point, viz. 5 atmospheres.

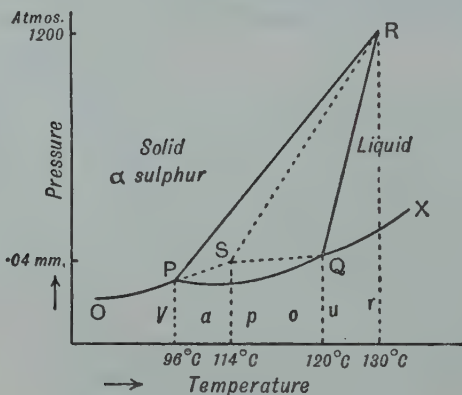


FIG. 40(a).

(4) Sulphur.

In Fig. 40 (a).

OP—Vapour pressure of rhombic sulphur at various temperatures.

PQ—Vapour pressure curve for monoclinic sulphur.

P is then the triple point for rhombic, monoclinic, and sulphur vapour, for at this point

$$\left. \begin{aligned} P + F &= C + 2 \\ 3 + F &= 1 + 2 \end{aligned} \right\} \therefore F = 0.$$

In the absence of a vapour phase $F = 1$, and we have the 'transition point' between rhombic and monoclinic varying with the pressure as shown by the line PR.

QX = boiling point curve.

Q is the triple point for monoclinic, vapour, liquid.

QR = melting point curve for monoclinic.

By rapid heating of rhombic sulphur beyond 96°C. (P) the metastable continuation of OP , viz. PS , can be followed until S is reached at 114°C.

S is then the triple point rhombic, vapour, liquid.

SR = melting point-pressure curve for rhombic	$\left\{ \begin{array}{l} SR, SQ \text{ are} \\ \text{both in the} \\ \text{metastable} \\ \text{area } PQR. \end{array} \right.$
SQ = boiling point curve—continuation of QX	

R is another triple point at which rhombic, monoclinic, and liquid sulphur are in equilibrium.

The triple points P, S, Q at 96°C. , 114°C. , and 120°C. each have their own *fixed* pressure. Thus the pressure corresponding to the point P is about 0.04 mm. In the case of this transition point (rhombic $\rightarrow$ monoclinic sulphur) an increase of pressure of 1 atmosphere only raises the transition point by about 0.05°C. Hence these triple point temperatures are practically the same as the transition point, the melting point of rhombic, and the melting point of monoclinic, respectively (all defined as at atmospheric pressure).

The allotropy of solid sulphur is of the type called **enantiotropy**, *i.e.* it is reversible.

On cooling liquid sulphur along XQ , monoclinic sulphur forms at Q , and on cooling this to P rhombic sulphur is formed. Instead of monoclinic crystals being formed at Q , supercooling may occur, *i.e.* the smooth curve, XQS is followed, the substance remaining liquid until rhombic sulphur crystallises out at S .

It will be seen that in this type of allotropy the transition point is **below** the melting point of either allotrope.

Fig. 40(b) illustrates a different case; one in which the transition point, if it could exist, would be **above** the melting points of the two solid allotropes.

One of the forms is metastable at all temperatures. A change can only occur in one direction, *i.e.* from the metastable to the stable form. This phenomenon is known as **monotropy**.

YQ is the vapour pressure curve for the solid stable form, and it cuts the vapour-pressure-liquid curve, XQ , at a triple point Q (approximating closely to the melting point of the stable form).

Similarly, OS is the vapour pressure curve for the metastable form and meets the vapour-pressure-liquid curve extended, at S (the melting point of metastable form under pressure of triple point). S may be reached if the liquid is cooled rapidly along XQ . Again if the vapour is chilled quickly it is possible to reach OS and obtain the metastable solid, *i.e.* by passing across YQ along a line such as ABC .

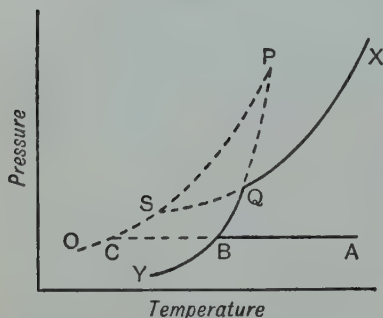


FIG. 40(b).

Phosphorus exhibits **monotropy**, the more active yellow form being unstable and the violet form stable. The change

from yellow, when once it is formed, to the stable violet variety may, however, be very slow unless accelerated by heating or by presence of a catalyst.

So-called yellow phosphorus (more correctly white phosphorus) is actually a solid solution of two allotropes both metastable and enantiotropic with respect to each other.

(5) *The Dissociation of Calcium Carbonate.*



As seen above, there are two components, two solid phases and one gaseous phase, and therefore the number of degrees of freedom is $2 + 2 - 3 = 1$. Thus if the temperature is fixed, then the pressure—the **dissociation pressure** of the carbon dioxide—is fixed.

This result can also be deduced from the Law of Mass Action (see page 153). If at a given temperature more carbon dioxide is forced into this system, then it will combine with lime to form calcium carbonate until the pressure of carbon dioxide is reduced to its

original value. If a stage is reached when all the lime is so converted, then one phase will have disappeared and there will be two degrees of freedom.

(6) Salt Hydrates.

The phase rule, applied to a system in which the number of components and degrees of freedom are known, will predict the number of phases, and hence throw light on the existence or formation of compounds.

Fig. 41(a) represents a curve showing the freezing points of solutions of ferric chloride in water plotted against the composition

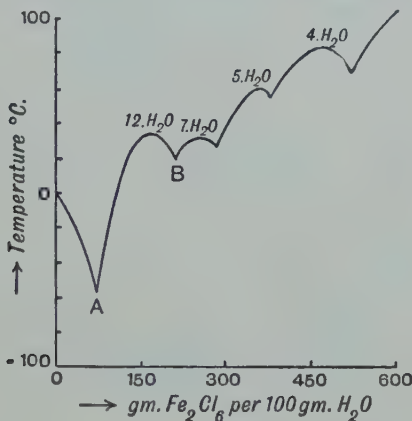


FIG. 41(a).—HYDRATES OF FERRIC CHLORIDE.

of the solid which crystallises out. It is important to notice that one degree of freedom has already been fixed in that the readings are those at constant pressure.

The sharp points on the diagram will therefore represent a system having this one degree of freedom, and since there are two components, there must be $2 + 2 - 1 = 3$ phases. The solution represents one phase, and hence there must be two solid phases, viz. either ice and $\text{Fe}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$ at A, or $\text{Fe}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$ and $\text{Fe}_2\text{Cl}_6 \cdot 7\text{H}_2\text{O}$ at B, etc., as eutectic mixtures.

The maxima on the curve represent the melting points of the pure compounds $\text{Fe}_2\text{Cl}_6 \cdot x\text{H}_2\text{O}$, etc., and x can be calculated from their position on the curve.

The use of the Phase Rule in determining the number of phases in a given system can be illustrated by Fig. 41(b), which gives the variation of vapour pressure with composition for the hydrates of copper sulphate.

The horizontal lines represent systems of two components, two solid and one vapour phase, and hence one degree of freedom, since

$$3 + F = 2 + 2.$$

As the diagram is drawn for constant temperature this degree of freedom is already fixed, and so, as long as two hydrates are present, the vapour pressure remains constant.

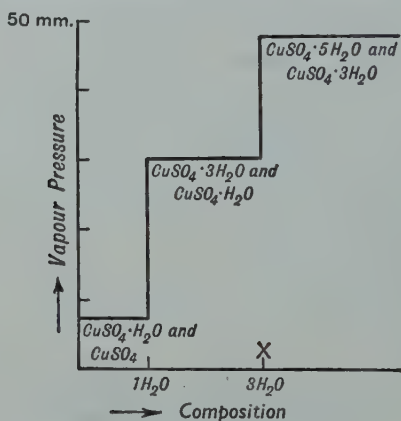


FIG. 41(b).

When one hydrate is present, *e.g.* the composition corresponds to X ($\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$), the vapour pressure shows a sudden change.

The 'Reduced' Phase Rule.

In dealing with equilibria between solids and liquids the effect of pressure is usually small, and in Figs. 35–38 it is assumed to be atmospheric and constant. Such systems, in which the vapour phase (under atmospheric pressure) does not exist, are known as 'condensed' systems.

The Reduced Phase Rule is then

$$p + F' = C + 1$$

where F' is the number of degrees of freedom which the system can possess in addition to the pressure.

For example, in Fig. 36, at the eutectic point C , we have, for this two-component system,

$$p + F' = 2 + 1$$

But there are, by physical inspection, two solid phases and one liquid phase; hence $F' = 0$ and C is a fixed invariant **point**—the pressure having been previously arbitrarily fixed as atmospheric.

Conversely, as C is a **point** there must be three phases, *i.e.* one liquid and two solid (eutectic) and not one solid (solid solution).

QUESTIONS ON CHAPTER IV.

Solubility.

1. Describe in detail how you would determine the solubility of oxalic acid in water.

2. The following data were obtained in experiments on the solubility of sodium sulphate :

Temp. ° C.	0°	10°	20°	30°	32.7°	35°	50°	100°
Solubility .	4.8	8.3	16.3	29.0	33.6	33.4	31.8	29.8

From these figures draw the solubility curve of sodium sulphate and discuss any abnormal characteristics which it possesses.

3. What is meant by the term 'saturated aqueous solution'? Explain the conditions under which it is possible to obtain from an aqueous solution of sodium sulphate (a) ice, (b) hydrated sodium sulphate, (c) anhydrous sodium sulphate. (Oxf. Schol.)

4. How may the solubility of salts in water be determined? The following figures record the solubility of sodium iodide in water at various temperatures. Plot a solubility diagram and discuss what information may be obtained from the curves.

Temperature (° C.).	Gms. NaI in 100 gms. solution.	Temperature (° C.).	Gms. NaI in 100 gms. solution.
140	77.0	30	65.5
120	76.3	10	62.8
100	75.4	-10	60.3
80	74.7	-15.2	57.2
60	72.0	-20	57.0
50	69.5	-30	40.0
40	67.2		

(Na = 23, I = 127.)

(Camb. Schol.)

5. Describe in outline how you would determine the solubility in water of ammonium chloride at the temperature of the laboratory.

The following weights of salt are dissolved by 100 gm. of water at the given temperatures :

Temp. ($^{\circ}$ C.).	KCl (gm.).	KClO ₃ (gm.).
0	28	3
50	42	19
100	56	59

Construct temperature-concentration diagrams approximately to scale and use them to show how you could best obtain more than 57 gm. of chlorate and some pure crystals of chloride from a solid mixture containing 59 gm. of chlorate and 14 gm. of chloride [Assume ideal experimental conditions.] (Camb. H.C.)

6. Phenol and water are said to combine to form a hydrate. How would you attempt to discover whether this is so, and determine its composition? (Oxf. Schol.)

7. Sulphuric acid is said to form solid hydrates of definite composition. How would you proceed to test this statement and to ascertain the composition of the hydrates? (Lond. H.C.)

Distillation of Liquid Mixtures.

8. Describe the behaviour of two non-miscible liquids on distillation. A mixture of ethylene dibromide and water boils at ordinary pressure at 91° C., the vapour pressure of water at this pressure being 545 mm. What will be the percentage composition of the distillate? (Camb. Schol.)

9. What are the general principles involved in fractional distillation? In the distillation of nitrobenzene by steam the mixture boils at 99° C. at a pressure of 760 mm. At this temperature the vapour pressure of water is 733 mm. The composition of the distillate is water : nitrobenzene :: 4 : 1. Calculate the molecular weight of the nitrobenzene from these data. (Camb. Schol.)

10. Describe and explain the operation known as distillation in steam. When aniline (mol. wt. = 93) is steam-distilled the distillate is found to contain 26.5% by weight of aniline. What is the approximate vapour pressure of aniline at the temperature of the distillation? (O. & C., H.C.)

11. Give an account with illustrative examples of (a) mixtures of constant boiling-point, and (b) distillation in steam. What are the advantages of the latter process?

The immiscible liquid system aniline-water boils at 98° C. under a pressure of 760 mm. At this temperature the vapour pressure of water is 707 mm. If this system is distilled in steam, what fraction of the total weight of the distillate will be aniline? (C.W.B., H.C.)

12. How would you distinguish between a pure liquid and a constant boiling-point mixture? Illustrate your answer by examples. (Camb. H.C.)

Partition Coefficient.

13. Discuss the theoretical and practical importance of the operation known as extraction with ether. Show that with a given quantity of ether it is more efficient to use small doses at a time.

14. Quote the law which describes the ratio in which a solute distributes itself between two immiscible solvents, and show how to derive the expression. How would you test the law in the case of iodine dissolving in water and benzene?

Prove that when a substance is being extracted from its aqueous solution by means, for example, of benzene, it is more economical to use a given volume of the latter in several fractions rather than as a whole. (Oxf. H.C.)

15. An aqueous solution contains 10 gm. of solute per litre; when 1 litre of the solution is treated with 100 c.c. of ether, 6 gm. of the solute are extracted. How much more of the solute would be extracted from the aqueous solution by a further 100 c.c. of ether? [Assume that the molecular state of the solute is the same in ether and water.] (Camb. H.C.)

16. Find the partition coefficient of oxalic acid between water and ether from the following data :

Grams oxalic acid per 10 c.c. water .	0.351	0.287	0.221
„ „ „ 10 c.c. ether .	0.039	0.032	0.0244

What will be the concentration of a litre of $\frac{N}{10}$ oxalic acid after shaking with (a) 1 litre of ether, (b) 2 litres of ether, and separating?

17. What general principles govern the distribution of a substance between two immiscible phases? Examine the following figures for the distribution of acetic acid between benzene and water from the point of view of the distribution law :

Conc. in benzene	0.043	0.071	0.094	0.149 gm. mol. per litre
Conc. in water	0.245	0.314	0.375	0.500

(Camb. Schol.)

18. Experiments on the ratio of distribution of phenol between water and chloroform gave the following results :

Aqueous solution	0.094	0.163	0.247	0.436
Chloroform solution	0.254	0.761	1.85	5.43

What conclusions may be drawn from these results regarding the molecular condition of phenol in chloroform solutions? (Camb. Schol.)

19. Describe one method for determining the 'partition coefficient' of a substance between two solvents. How may this determination give evidence of the presence of complex molecules? (Oxf. Schol.)

Solubility of Gases.

20. How would you proceed to determine the solubility of (a) ammonia, (b) oxygen in water?

Discuss the effect of (a) temperature, (b) pressure on the solubility of a gas.

21. How would you determine as accurately as possible the amount of carbon dioxide that dissolves when a current of the gas is bubbled through water at room temperature? Give full experimental details.

What grounds have we for thinking that combination takes place between carbon dioxide and water? (Oxf. H.C.)

22. What are Henry's Law and Dalton's Law of partial pressures? Explain what is meant by the distribution coefficient, and discuss the relationship between this quantity and the two laws mentioned. (Camb. Schol.)

23. How is the *absorption coefficient* of a gas defined?

How would you measure the solubility in water of (a) oxygen, (b) hydrogen chloride? (Camb. H.C.)

24. On what factors does the solubility of a mixture of gases depend? At N.T.P. 1.0 c.c. of water dissolve 0.0489 c.c. of oxygen and 0.0235 c.c. of nitrogen. Supposing that air consists of 79% of nitrogen and 21% of oxygen by volume, calculate the percentage composition by volume at N.T.P. of the gas dissolved from air by water. (N.U.J.B.)

25. One litre of water is shaken with a large volume of a gas which consists of 50% nitrogen, 45% oxygen, and 5% carbon dioxide. Assuming that the composition and pressure of the gas are not materially altered during the process, calculate the volume and percentage composition of the dissolved gas.

(Coefficients of solubility: nitrogen, 0.015; oxygen, 0.03; carbon dioxide, 1.0.) (Oxf. H.C.)

26. State the law of partial pressures and explain its application in correcting for the pressure of water vapour in a volume of gas collected over water.

A 2-litre globe containing oxygen under a pressure of 2 atmospheres was put into communication with a 4-litre globe containing nitrogen at 0.25 atmosphere, and the gases were allowed to mix. Calculate (a) the total pressure, (b) the pressure of oxygen in the system assuming that no change of temperature has taken place. (Camb. 1st M.B.)

27. How may the solubility of a gas in a liquid be determined? What is the absorption coefficient, and how may it be modified when (a) mixed gases, (b) solutions instead of pure liquids are employed? The concentrations of chlorine gas c_1 in millimol. per litre over a carbon tetrachloride solution of concentrations c_2 at 0°C. are as follows:

c_1	.	.	.	0.0554	0.0889	0.1341	0.1760
c_2	.	.	.	4.454	7.490	11.035	15.200

What conclusions can be drawn as to the state of the chlorine in the carbon tetrachloride? (Camb. Schol.)

Solubility Curves—The Phase Rule.

28. The data below represent the temperatures at which solid begins to separate from fused alloys of zinc and antimony of the composition shown :

Pure Zn	443° C.	30% Sb	535° C.	75% Sb	507° C.
2% Sb	420° C.	40% Sb	553° C.	80% Sb	510° C.
5% Sb	428° C.	50% Sb	565° C.	90% Sb	561° C.
10% Sb	456° C.	60% Sb	566° C.	Pure Sb	632° C.
20% Sb	502° C.	70% Sb	530° C.		

Plot these figures on squared paper. What can you infer from the graph? What would happen if an alloy with 65% antimony were gradually heated from 400° to 600°? (Oxf. Schol.)

29. Solutions of common salt in water may be in equilibrium with crystals of salt or ice or both. Draw the form of the curves representing the relation between temperature and the concentration of the solution in equilibrium with (a) ice, and (b) salt. Explain every part of the diagram. Comment on the term cryohydrate. Explain why ice and salt provide a good freezing mixture. (C.W.B., H.C.)

30. Explain the terms 'phase,' 'number of components,' degrees of freedom. State the Phase Rule and apply it to elucidate the dissociation of calcium carbonate.

31. Give an account, in terms of the Phase Rule, of the system sodium chloride-water.

32. What do you understand by a 'triple point'? Illustrate your answer by examples.

33. Copper sulphate crystals consist of the pentahydrate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. How would you attempt to discover experimentally whether copper sulphate forms a hydrate or hydrates containing a smaller number of molecules of water of crystallisation? (N.U.J.B., H.C.)

34. An anhydrous salt is left in contact with water vapour, with which it unites to form several hydrates. How would you show the existence of these hydrates and determine their composition? (Camb. Schol.)

35. Write a short essay on the Phase Rule. (Camb. Schol.)

CHAPTER V

OSMOTIC PRESSURE AND ALLIED PHENOMENA

A STRONG solution of a coloured salt, such as copper sulphate, if placed carefully at the bottom of a cylinder of water, will be found to diffuse gradually so as to make the whole of uniform colour. Further, if a membrane, through which only water can pass, separates a solution from the water, a phenomenon related to diffusion occurs. The passage of water through the membrane brings about dilution of the solution and a very considerable pressure can be shown to exist.

This phenomenon is known as *osmosis*, and the pressure which is observed is called the *osmotic pressure* of the solution.

In 1748 the Abbé Nollet found that if a bladder containing alcohol was immersed in water, the latter diffused into the alcohol until the bladder burst. An egg from which the shell has been dissolved by dilute acid will swell if immersed in water, but will shrink if immersed in strong salt solution. In the latter case the solution outside is stronger than that inside, and water diffuses out of the egg. Similar effects were observed with plant cells, by De Vries in 1888, and any solutions which produce neither swelling nor shrinking of a particular plant cell are said to be *isotonic*.

The fact that osmotic pressures may be very high is readily shown by tying a piece of parchment over the mouth of a thistle funnel containing strong copper sulphate solution and immersing the apparatus in a beaker of water. The water passes through the parchment and the blue solution (gradually becoming, of course, more dilute) rises a considerable distance up the extended stem of the funnel until its hydrostatic pressure balances the osmotic pressure.

Membranes which allow the solvent but not the dissolved molecules of solute to pass through them are called *semi-permeable*.

A crystal of potassium ferrocyanide when dropped into a solution of copper sulphate will begin to dissolve, forming a strong

solution of potassium ferrocyanide surrounding the crystal. As this is in contact with copper sulphate, a thin film of the insoluble red-brown copper ferrocyanide will be formed. This acts as a semi-permeable membrane, which swells often more in one direction than another, producing quaint, plant-like growths. A more spectacular '**chemical garden**' is produced if small crystals of various inorganic salts, copper sulphate, nickel sulphate, alum, etc., are dropped into a somewhat viscous solution of water glass, sodium silicate (5% solution).

Measurement of Osmotic Pressure.

The essential requirement is a membrane, which is as perfectly semi-permeable as possible, arranged so as to withstand the high pressures which are exerted upon it. There have been three principal quantitative investigations of the phenomenon of osmotic pressure :

(a) *Pfeffer* (c. 1877).

Pfeffer used a porous pot of unglazed earthenware, which had been carefully cleaned, filled with potassium ferrocyanide solution and placed in a solution of copper sulphate. Thus a copper ferrocyanide membrane was produced inside the pores of the pot and was therefore fairly rigid.

A side tube connected the pot to a closed manometer containing mercury and also nitrogen whose changes of volume recorded the pressures produced.

The pot and the space between it and the mercury were filled with the solution. A tightly fitting cap was placed in the top of the pot, and any excess of solution escaped through the jet *J* which was finally sealed off (see Fig. 42).

Pfeffer thus discovered the following laws—using a solution of cane-sugar :

Laws of Osmotic Pressure.

1. The osmotic pressure is proportional to the concentration of the solution, if the temperature is kept constant.

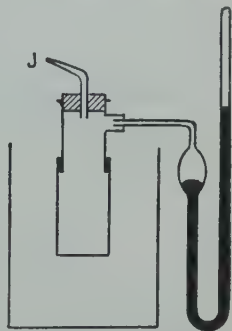


FIG. 42.—PFEFFER'S METHOD FOR MEASURING OSMOTIC PRESSURE.

2. For a given solution the osmotic pressure is proportional to the absolute temperature.

Some of Pfeffer's experimental results are given in the two tables below :

TABLE I.

Conc. of cane-sugar, C in gm. per 100 c.c.	Osmotic Pressure, P in cm. of mercury.	$\frac{P}{T}$
1	53.5	53.5
2	101.6	50.8
4	208.2	52.0
6	307.5	51.3

TABLE II.

Temperature in ° C.	Osmotic Pressure, P in cm. of mercury.	Temperature in ° Absolute.	$\frac{P}{T}$
14.2	53.1	287.2	0.185
22.0	54.8	295	0.186
6.8	50.5	279.8	0.181
13.2	52.1	286.2	0.182

These results were for a 1% sugar solution.

These results were sufficiently accurate to enable *van 't Hoff* (1887) to formulate a theory of solution, postulating that the molecules of dissolved substance behave as those of a perfect gas occupying the space of the solution.

In Law 1 if instead of using

C = conc. in gm. per 100 c.c.

we use V = volume containing 1 gm.

then we obtain $P \times V$ = a constant, when T is constant

Combining this with Law 2 :

$$\frac{P}{T} = \text{a constant when } V \text{ is constant.}$$

we obtain
$$\frac{P \times V}{T} = \text{a constant or } PV = kT.$$

Moreover, if the volume of solution V is written as that which

contains 1 gram-molecule of solute, then the constant k is found to be the same for all dissolved substances (exceptions see below) and equal to the constant R in the general gas equation $PV = RT$.

Thus when V is equal to 22.4 litres and T is equal to 273° Abs. then P is equivalent to a pressure of 76 cm. of mercury.

Calculation of Molecular Weights from Osmotic Pressures.

Using Pfeffer's experimental data we have that 1 gm. of cane-sugar in 100 gm. of water (approx. 100 c.c. solution) gives an osmotic pressure of 53.1 cm. at 14.2° C.

Let M = mol. wt. of cane-sugar, then we know in general that : M gm. in 22,400 c.c. at 0° C. (273° Abs.) give osmotic pressure of 76 cm.

$$\therefore 1 \text{ gm. in } 100 \text{ c.c. at } 273^\circ \text{ abs. gives } 76 \times \frac{1}{M} \times \frac{22,400}{100} \text{ cm.}$$

$$\therefore 1 \text{ gm. in } 100 \text{ c.c. at } 14.2^\circ \text{ C. (} 287.2^\circ \text{ abs.) gives}$$

$$76 \times \frac{1}{M} \times \frac{22,400}{100} \times \frac{287.2}{273} \text{ cm.} = 53.1 \text{ cm.}$$

$$\therefore M = \frac{76}{53.1} \times 224 \times \frac{287.2}{273} = 338$$

Actually the molecular weight of cane-sugar is 342.

The student will find that it is safer to work out results from first principles, as above, rather than to attempt to memorise a formula.

Difficulties in Measuring Osmotic Pressures.

1. A perfect semi-permeable membrane cannot be made.
2. The membrane has to stand up to very high pressures.
3. A long time elapses before the pressure reaches its maximum value.

For these reasons other methods (see later) are preferred for finding molecular weights. Improvements have been made on the original apparatus of Pfeffer.

(b) *Morse and Frazer* (c. 1910).

These workers used more efficient porous pots and an electric current to facilitate the deposition of the copper ferrocyanide membrane. Their results showed closer agreement with the gas laws than those of Pfeffer, for dilute solutions, but considerable divergences in the case of stronger solutions.

The divergence is still marked, though less pronounced, if the solute molecules are regarded as occupying the volume of the solvent and not of the solution.

As in the case of gases it is found that for concentrated solutions the product PV increases rapidly as the osmotic pressure increases.

(c) *Berkeley and Hartley.*

These workers obtained still more reliable results by measuring pressures which must be applied to counteract osmosis.

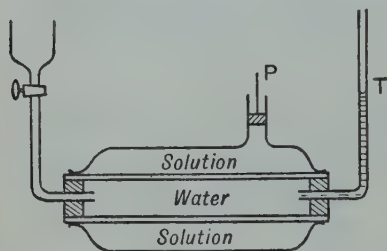


FIG. 43.—METHOD OF BERKELEY AND HARTLEY FOR MEASURING OSMOTIC PRESSURE.

The apparatus is shown diagrammatically in Fig. 43.

A porous pot, surrounded by the solution, contains water connected to a capillary tube T . The passage of water through the pot is opposed by the application of a hydraulic pressure, which can be measured, at P . The pressures necessary so that water just passes one way and then the other through the

porous pot are observed. Their mean is taken as the osmotic pressure. The passage of the water is indicated by a slight rise or fall of the meniscus in the tube T .

Abnormal Results for Osmotic Pressure.

In many cases van 't Hoff found it necessary to introduce a factor ' i ' into his equation, thus $PV = iRT$, in order to give consistent results.

If ' i ' is less than unity, then it implies that the number of effective molecules is less than expected theoretically, and may therefore represent '**association**' of the dissolved molecules.

Conversely, if ' i ' is greater than one, and this is found to be so in the case of electrolytes, the result can be explained in terms of '**ionisation**' or '**electrolytic dissociation**' (see Chapter VIII).

' i ' will be an integer only when ionisation is complete. In other cases the degrees of ionisation may be calculated.

Degrees of Ionisation.

The degree of ionisation is defined as the fraction of the total number of original molecules which are split up into ions.

Thus if α is the degree of ionisation in the case of a binary electrolyte (*i.e.* one whose molecule can form two ions), there will be α ions of each sort in the place of one original molecule, leaving $1 - \alpha$ molecules undissociated.

The number of 'effective molecules' in the place of one original molecule will therefore be $1 - \alpha + 2\alpha = 1 + \alpha$ and $i = \frac{1 + \alpha}{1}$.

A salt such as $\text{Ca}(\text{NO}_3)_2$ will give $\overset{++}{\text{Ca}}$ and 2NO_3^- , $\text{Al}_2(\text{SO}_4)_3$ will give $2\overset{+++}{\text{Al}}$ and 3SO_4^{--} , and in general if one molecule gives m ions, we shall have $1 - \alpha + m\alpha$ effective molecules.

$$\therefore \frac{1 - \alpha + m\alpha}{1} = i \quad \text{or} \quad \alpha = \frac{i - 1}{m - 1}$$

Expressed as a percentage the degree of ionisation will of course be 100α .

*It is more correct to use the expression **apparent degree of ionisation** (see p. 179).*

Example.

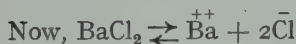
The osmotic pressure of a solution containing 10 gm. of barium chloride, BaCl_2 , per litre is found to be 3.2 atmospheres at 15°C . Calculate the apparent degree of ionisation of the barium chloride in this solution.

Molecular weight of $\text{BaCl}_2 = 137 + 71 = 208$.

Hence 208 gm. BaCl_2 in 22,400 c.c. at 0°C . give (if non-dissociated) osmotic pressure 1 atmos.

$\therefore$ 10 gm. BaCl_2 in 1000 c.c. at 15°C . give (if non-dissociated) osmotic pressure of:

$$\frac{10}{208} \times \frac{22,400}{1000} \times \frac{288}{273} \text{ atmos} = 1.136 \text{ atmos.}$$



$\therefore$ $1 - \alpha$ α 2α represent effective particles if α is the apparent degree of ionisation.

Total effective particles = $1 - \alpha + \alpha + 2\alpha = 1 + 2\alpha$.

$$\begin{aligned} \therefore \frac{\text{Observed Pressure}}{\text{Normal calculated pressure}} &= \frac{1 + 2\alpha}{1} = \frac{3.2}{1.136} \\ \therefore 2\alpha + 1 &= 1 + \frac{2.064}{1.136} \\ \therefore \alpha &= \frac{1.032}{1.136} = 0.91 \text{ i.e. } 91\% \text{ dissociated.} \end{aligned}$$

The Nature of Osmotic Pressure.

Many explanations to account for the phenomena of osmosis have been suggested, but no agreement has yet been reached.

One popular view is that water can dissolve in the membrane,

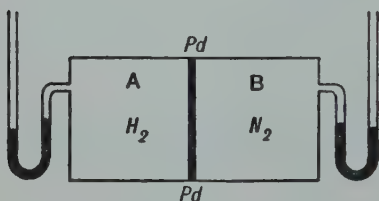


FIG. 44.

whilst the dissolved substance cannot do so. The water therefore diffuses through the membrane until its partial pressure on the two sides is the same.

This is supported by Ramsay's experiment using palladium (in which hydrogen dissolves) as a membrane to

separate the gases hydrogen and nitrogen. The apparatus is shown in diagrammatic form in Fig. 44. Two equal vessels, A and B, separated by a palladium diaphragm, Pd, contain hydrogen and nitrogen respectively at atmospheric pressure, P , as recorded on the two pressure gauges. When the palladium is heated, hydrogen diffuses through until its partial pressure becomes $\frac{P}{2}$ on each side.

The right-hand gauge will then register a pressure of $\frac{3P}{2}$ compared with $\frac{P}{2}$ and the difference, viz. P , represents the 'osmotic pressure of the nitrogen.'

To regard osmotic pressure as due to bombardment by solute molecules is clearly misleading. A glass bottle containing a solution of very high osmotic pressure does not burst, for this osmotic pressure does not exist unless a semi-permeable membrane is present separating the solution from solvent.

The *osmotic pressure* is best defined as the pressure which must be exerted to prevent solvent molecules from passing through a semi-permeable membrane into the given solution.

Osmotic Pressure and Vapour Pressure.

Fig. 45 represents a thistle funnel and stem containing a solution separated from pure solvent by a semi-permeable membrane. This apparatus is supposed to be enclosed in an evacuated bell-jar, at constant temperature. Equilibrium is attained when the pressure of the column of solution of height h is equal to the osmotic pressure P .

The vapour pressure of the pure solvent is p , and this must be the pressure at a point X near the surface of the solvent.

The vapour pressure of the solution is p_1 , and this must be the pressure at a point Y , and also at a point Z in the same horizontal line as Y .

If d is the density of the vapour, then the difference of pressure between X and Z is

$$p - p_1 = h \times d \quad . \quad (i)$$

If s_1 is the density of the solution, then osmotic pressure

$$P = h \times s_1 = h \times s$$

$$\therefore h = \frac{P}{s} \quad . \quad . \quad . \quad (ii)$$

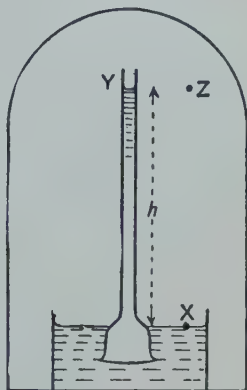


FIG. 45.

where s is the density of the pure solvent, since for dilute solutions $s = s_1$. For the vapour of the pure solvent $pv = RT$, where v is the gram-molecular volume which is equal to $\frac{M}{d}$, where M is the molecular weight.

$$\text{Hence} \quad p \times \frac{M}{d} = RT \text{ or } p = RT \times \frac{d}{M} \quad . \quad . \quad (iii)$$

$\therefore$ From, equations (i) and (iii)

$$\frac{p - p_1}{p} = h \times d \times \frac{M}{RTd} = \frac{h \times M}{RT}$$

Substituting the value of h from equation (ii), we obtain

$$\frac{p - p_1}{p} = P \times \frac{M}{s \times RT} \quad . \quad . \quad . \quad (iv)$$

This expression $\frac{p - p_1}{p}$ is called the relative lowering of the vapour pressure of the solvent due to the presence of the solute. Moreover, for a given solvent, at a given temperature, $\frac{M}{s \times RT}$ is a constant.

Therefore the relative lowering of the vapour pressure is proportional to the osmotic pressure.

Further, if n gm.-mol. of solute are present in N gm.-mol. of solvent

$$= NM \text{ gm.} \quad ,,$$

$$= \frac{NM}{s} \text{ c.c.} \quad ,,$$

then 1 gm.-mol. of solute is present in $= \frac{NM}{ns} \text{ c.c.} \quad ,,$

The osmotic pressure is given by the gas law equation $P \times v = RT$, where v = volume of solvent occupied by 1 gm.-mol. of solute, viz. $\frac{NM}{ns}$.

$$\therefore P = \frac{RT}{v} = \frac{RT}{1} \times \frac{ns}{NM}$$

$$\therefore \frac{p - p_1}{p} = \frac{P \times M}{sRT} \text{ (see equation iv)} = \frac{RTns}{NM} \times \frac{M}{sRT} = \frac{n}{N}$$

If in proving the above, the density of the solution is not assumed to be equal to that of the solvent the following expression is obtained :

$$\frac{p - p_1}{p} = \frac{n}{N + n}$$

$$\text{i.e. Relative Lowering} = \frac{\text{Number of solute molecules}}{\text{Number of solvent molecules} + \text{Number of solute molecules}}$$

Raoult's Law.

The above relationship was experimentally established, for certain solutions, by Raoult in 1887, and is usually known as Raoult's Law.

The fundamental assumption is that in an *ideal solution* (i.e. one which obeys Raoult's law) the vapour pressure of the solvent molecules above such a solution will depend only on the ratio of

the number of solvent molecules to the total number of molecules present in the solution.

$$\text{Hence} \quad p_1 = k \frac{N}{N+n}$$

For pure solvent $p_1 = p$, $\frac{N}{N+n} = 1$, and so $k = p$.

$$\text{Thus} \quad \frac{p - p_1}{p} = \frac{k - k \frac{N}{N+n}}{k} = \frac{n}{N+n}$$

Molecular Weights from Lowering of Vapour Pressure, etc.

The relative lowering of vapour pressure and other properties (such as depression of freezing-point and elevation of boiling point) which are directly proportional to it, and therefore to osmotic pressure, are capable of easier and more accurate experimental measurement than osmotic pressure. They are therefore used for the determination of molecular weights in solution.

Thus if w and m are the weight and molecular weight of solute dissolved in W gm. of solvent of molecular weight M , the above equation becomes

$$\frac{p - p_1}{p} = \frac{n}{N+n} = \frac{\frac{w}{m}}{\frac{W}{M} + \frac{w}{m}}$$

and if m is the only unknown in this equation it can be calculated.

Experimental Measurement of Lowering of Vapour Pressure.

Ostwald's Method.

A series of bulbs containing solution and a series containing pure solvent are connected together as shown in Fig. 46.

Each series is separately weighed and a slow current of air is passed through for some time.

The air will first become saturated with water vapour to an extent depending on the vapour pressure of the solution, viz. p_1 , and

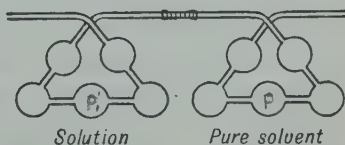


FIG. 46.—OSTWALD'S METHOD FOR MEASURING LOWERING OF VAPOUR PRESSURE.

then, in the second set of bulbs, to a further extent depending on that of the pure solvent p .

On reweighing, the first bulb will lose weight w_1 proportional to p_1 , and the second will lose *further* weight w_2 proportional to $p - p_1$. $w_1 + w_2$ will, moreover, represent the weight which would be lost in saturating the dry air if passed through the pure solvent only. This will in fact be the gain in weight of a third series of bulbs containing a drying agent, if attached to the end of the above apparatus.

Thus
$$\frac{p - p_1}{p_1} = \frac{w_2}{w_1}$$

$$\therefore \frac{p}{p_1} - 1 = \frac{w_2}{w_1} \quad \text{or} \quad \frac{p}{p_1} = \frac{w_2 + w_1}{w_1}$$

$$\therefore \frac{p_1}{p} = \frac{w_1}{w_2 + w_1} \quad \therefore \frac{p_1}{p} - 1 = \frac{w_1}{w_2 + w_1} - 1 = \frac{-w_2}{w_2 + w_1}$$

$$\therefore \frac{p - p_1}{p} = \frac{w_2}{w_2 + w_1}$$

This gives the relative lowering if w_1 and w_2 are measured.

Alternatively $\frac{p - p_1}{p} = \frac{w_2}{W}$ where $W = w_2 + w_1$

This expression is used if W is measured in a third series of bulbs.

Example.

A current of dry air was bubbled through a bulb containing a solution of 14.63 gm. of urea per 100 gm. water, then through a bulb containing pure water, and finally through a bulb containing strong sulphuric acid. The loss of weight of the water-bulb was 0.087 gm. and the gain of weight of the sulphuric acid bulb was 2.036 gm. Calculate the molecular weight of the urea.

Now, p is $\propto$ gain of weight of sulphuric acid bulb

and $p - p_1$ is $\propto$ loss of weight of water-bulb, since the air was previously saturated with water-vapour, to pressure p_1 in the urea solution.

$$\therefore \frac{p - p_1}{p} = \frac{0.087}{2.036}$$

Also if m = molecular weight of urea, and since 18 = molecular weight of water, we have

$$\frac{n}{N+n} = \frac{\frac{14.63}{m}}{\frac{100}{18} + \frac{14.63}{m}} = \frac{p - p_1}{p} = \frac{0.087}{2.036}$$

Inverting these fractions we have :

$$\left(\frac{100}{18} \times \frac{m}{14.63} \right) + 1 = 1 + \frac{1.949}{0.087}$$

$$\therefore m = \frac{1.949}{0.087} \times \frac{18 \times 14.63}{100} = 59.0.$$

The Elevation of the Boiling Point.

Since the vapour pressure of a solvent is lowered by the presence of solute, and since a liquid will not boil until its vapour pressure is equal to that of the atmosphere above it, then it follows that its boiling point will be raised.

The vapour pressure-temperature curves for a solvent when pure and when it contains small quantities of solute are practically parallel, and therefore the elevation of the boiling point is *proportional* to the lowering of vapour pressure. This relationship is easily seen to be true in Fig.

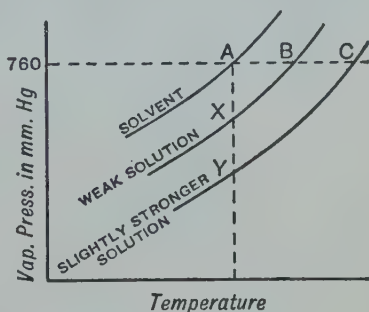


FIG. 46(a).

46(a) in which the vapour-pressure-temperature curves are shown for pure solvent and for two dilute solutions of a substance in this solvent.

The points on these curves corresponding to a pressure of 760 mm. mercury represent the boiling points A, B and C of the liquids.

The lowerings of vapour pressure are AX and AY.

The elevations of boiling point are AB and AC.

Assuming the curves to be parallel for dilute solutions in the neighbourhood of their boiling points

$$\frac{AB}{AC} = \frac{AX}{AY}.$$

Thus if t_0 = boiling point of solvent and t_1 = boiling point of solution then :

$$t_1 - t_0 = k_1(p - p_1)$$

But $\frac{p - p_1}{p} = \frac{n}{N + n}$ and p is a constant for a given solvent.

$$\therefore t_1 - t_0 = k_2 \frac{n}{N + n} = k_2 \frac{n}{N} \text{ for small values of } n$$

$$= k_2 \frac{\frac{w}{m}}{W} = k_3 \cdot \frac{w}{mW}, \text{ since } M \text{ is constant.}$$

Hence the elevation of the boiling point is proportional to the weight, w , of solute, inversely proportional to its molecular weight, m , and inversely proportional to the weight, W , of solvent.

This result was also arrived at independently, by Raoult, by experimental methods.

TABLE III.

Typical Solvents.	Molecular Elevation of the Boiling Point for 1 gm.-molecule in 100 gm. Solvent. K.
Water	5.2° C.
Acetone	17.2° C.
Ether	21.1° C.
Benzene	25.7° C.
Ethyl Alcohol	11.5° C.
Chloroform	38.8° C.

In order to calculate the molecular weight, m , of a solute the constant must be known for the given solvent, and this may be experimentally determined using a solute of known molecular weight. It can also be calculated theoretically (see page 129).

The *molecular elevation of the Boiling-Point Constant* (ebullioscopic constant) is often defined as *the elevation of the boiling point of the given solvent which would be produced by 1 gm.-molecule of any solute* (if not associated nor dissociated) *in 100 gm. of solvent*.

Thus the Boiling-Point Constant K is the value of $t_1 - t_0$ when $\frac{w}{m} = 1$, and $W = 100$, i.e. $K = \frac{k_3}{100}$ (see above), and elevation of boiling point $= k_3 \frac{w}{mW} = \frac{100Kw}{mW}$.

The above definition is open to the objection that in most cases 1 gm.-molecule will not dissolve in 100 gm. of solvent, and even if it does, the solution would be too concentrated to obey the simple law that elevation is proportional to concentration. Provided that this is clearly understood, the constant is quite convenient in calculating results. These constants are, however, sometimes written as referring to 1000 gm. of solvent, and the student must be on his guard for this.

Experimental Measurement of Boiling-Point Elevation.

Beckmann's Method.

A known weight of solvent is contained in the inner vessel, A , Fig. 47; and this is surrounded by vapour of boiling solvent contained in the vessel BB . Both vessels are connected to condensers to prevent loss of vapour.

Small known weights of the solute (in pellet form if solid) are added through the side tube.

The errors due to superheating are minimised by having some small beads of agate or glass in the boiling tube A and a piece of platinum wire fused through the bottom of the tube.

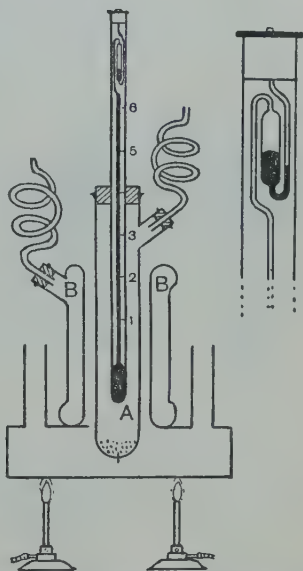


FIG. 47.—BECKMANN'S METHOD FOR MEASURING ELEVATION OF BOILING POINT.

Heat is conducted through this wire and small bubbles of vapour form more easily on it and on the beads.

Since the elevations to be measured must be those for dilute solutions, and are therefore small, a Beckmann thermometer is used.

This possesses a very fine stem with a temperature range of only 6°C . The approximate temperature at which this range is required can be obtained by adjusting the amount of mercury in the thermometer relative to that in the reservoir at its upper end. More mercury can be obtained from the reservoir by raising the temperature until the thread reaches the reservoir, and on cooling more mercury can be drawn back with the retreating thread.

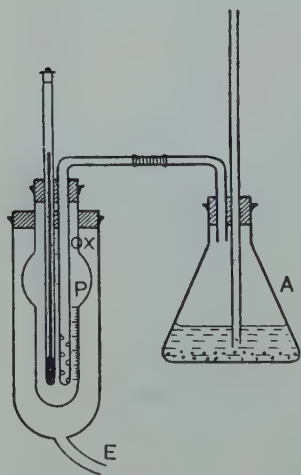


FIG. 48. — LANDSBERGER'S METHOD FOR MEASURING ELEVATION OF BOILING POINT.

Landsberger's Method.

In this method, of which there are various modifications, vapour from the boiling solvent in a separate heater, *A*, is passed through a glass tube, perforated with holes, into the inner vessel, *P* (see Fig. 48). The vapour at first condenses, and, when the boiling point is reached, it passes through unchanged, issuing from the hole *X* to form a vapour jacket to the inner tube. It finally escapes through the exit *E*.

The inner tube is graduated and has an enlargement towards the top to prevent loss of liquid by splashing through *X*.

This method of heating the liquid keeps the latter well stirred and diminishes the chances of superheating.

After the boiling point of the pure solvent has been determined, a small amount of liquid is left in the tube *P* and a weighed quantity of solute is added. When the supply of vapour is renewed it condenses in the solution, giving up its latent heat until the solution boils, when the vapour will again pass through without condensing. The boiling point is now read, the supply of vapour

being stopped for a short time whilst the volume of solution is read off on the graduated scale.

By this time the solution will have cooled down somewhat, and on further heating more vapour will condense. The solution thus becomes weaker and a new boiling point can be observed for a correspondingly increased volume of solution.

Thus several readings can be obtained quite quickly. Owing to the space occupied by the thermometer, etc., the volumes as recorded must be converted into actual volumes by filling up to the observed levels with water from a burette.

In calculating results from this method, it should be noted that the ebullioscopic constant required is K_1 , referring to **100 c.c.** of solvent and not K which refers to **100 gm.** Clearly $K_1 = \frac{K}{d}$, where d is the density in gm. per c.c. of the solvent at its boiling point.

Example.

The boiling point of pure acetone is 56.38°C . A solution of 0.707 gm. of a compound in 10 gm. of acetone boiled at 56.88°C . What is the molecular weight of the compound if the molecular elevation constant for acetone is 17.2°C .?

Then m gm. (m = mol. wt.) of substance in 100 gm. acetone give elevation of 17.2°C .

$\therefore$ 1 gm. of substance in 1 gm. acetone gives elevation of

$$\frac{17.2}{m} \times \frac{100}{1}$$

$\therefore$ 0.707 gm. of substance in 10 gm. acetone give elevation of

$$\frac{17.2}{m} \times \frac{100}{10} \times 0.707^\circ \text{C.} = 0.5^\circ \text{C. (i.e. } 56.88 - 56.38)$$

$$\therefore m = \frac{17.2 \times 7.07}{0.5} = 243$$

The Depression of the Freezing Point.

As in the case of the elevation of the boiling point, it can similarly be shown that the depression of the freezing point of a solvent is proportional to the lowering of vapour pressure, which is itself proportional to the osmotic pressure.

In Fig. 48(a), *A*, *B* and *C* represent the freezing points of the pure solvent and two dilute solutions. At each freezing point the vapour pressure of the solution must be equal to that of pure solid solvent, since they are in equilibrium.

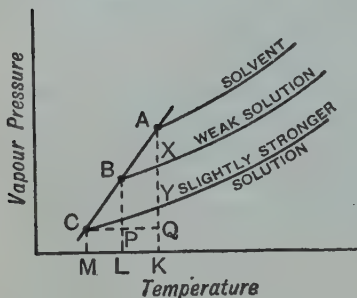


FIG. 48(a).

Thus *ABC* is the vapour-pressure curve of pure solid solvent.

Lowerings of vapour pressure are *AX* and *AY*.

Depressions of freezing point are *KL* and *KM*, and :

$$\frac{KL}{KM} = \frac{QP}{QC} = \frac{AB}{AC} = \frac{AX}{AY}.$$

By reasoning similar to that on page 124 we have :

Depression of Freezing Point = $k \times \frac{w}{mW}$, where *w* = weight of solute, *W* = weight of solvent, *m* = molecular weight of solute, and *k* is a constant depending on the solvent.

Again, this result was also developed experimentally. **Blagden's Law**, (1788) states that the depression of the freezing point is proportional to the concentration of the solute. Raoult (1883) showed that the depression was also inversely proportional to the molecular weight of the solute.

Thus the **Freezing-Point Depression Constant** (cryoscopic constant) is usually defined as **the depression of the freezing point of the solvent which would be produced by 1 gm.-**

TABLE IV.

Typical Solvents.	Molecular Depression of the Freezing Point for 1 gm.-molecule in 100 gm. Solvent. <i>K</i> .
Water	18.5° C.
Acetic Acid	39° C.
Benzene	51.2° C.
Phenol	53° C.
Camphor	400° C.

molecule of any solute (if not associated nor dissociated) **in 100 gm. of the solvent.**

It should be noted that this definition is open to similar objections to those mentioned on page 125.

Relation between Elevation and Depression Constants and Latent Heat.

Although both these constants may be determined experimentally for a given solvent, using a suitable solute of known molecular weight, they can also be calculated theoretically.

From thermodynamics it can be shown that :

the constant as defined above $= \frac{2T^2}{100L}$

where T = the freezing point or boiling point of the pure solvent in ° Absolute and L = the latent heat of fusion or evaporation of the solvent in calories per gm.

Thus for water $T = 273$ and $L = 80$.

$$\therefore \text{Freezing-Point Depression Constant} = \frac{2 \times 273 \times 273}{8000} \\ = \underline{18.6^\circ \text{C.}}$$

This agrees closely with the experimental value 18.5°C.

Experimental Measurement of Freezing-Point Depressions.

Beckmann's Method.

The apparatus, shown in Fig. 49, consists of an inner tube, fitted with a Beckmann thermometer, side tube, and stirrer, enclosed by an outer tube. The space between the tubes forms an air-jacket, and the whole apparatus is surrounded by a suitable freezing bath, depending on the freezing point of the solvent.

A known weight of pure solvent is placed in the inner tube and its freezing point determined.

A known weight of solute (in pellet form if a solid) is added through the side tube.

The new freezing point is determined. Supercooling will probably occur even if the solution is well stirred, but when crystallisation of solvent begins, the temperature will rise again to the true freezing point.

It is important that the freezing-point temperature should

be read when only a small number of crystals are present, otherwise it will correspond to a solution stronger than that assumed from the weights of substances originally taken.

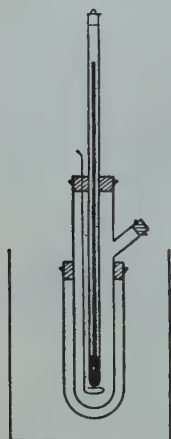


FIG. 49. — APPARATUS FOR MEASURING DEPRESSION OF FREEZING POINT.

Examples.

1. The freezing point of a solution containing 1 gm. of a sugar per 100 c.c. solution is -0.105° C. Calculate the molecular weight of the sugar.

Let m = mol. wt. of sugar.

Then m gm. sugar in 100 gm. water (i.e. 100 c.c. solution) give depression 18.5° C.

$\therefore$ 1 gm. sugar in 100 gm. water (i.e. 100 c.c. solution) gives depression $\frac{18.5}{m}$

$$\therefore \frac{18.5}{m} = 0.105 \quad \therefore m = \frac{18.5}{0.105} = 176$$

2. A solution containing 6.828 of sodium nitrate, NaNO_3 , in 100 gm. of water freezes at -2.44° C. Calculate the apparent degree of ionisation of the sodium nitrate.

Mol. wt. of $\text{NaNO}_3 = 23 + 14 + 48 = 85$.

$\therefore$ 85 gm. NaNO_3 in 100 gm. water gives depression of 18.5° C. (if not dissociated).

$\therefore$ 6.828 gm. NaNO_3 in 100 gm. water give depression, in $^{\circ}$ C., of

$$\frac{18.5 \times 6.828}{85} = 1.486.$$

If α = degree of ionisation then :

$$\frac{1 + \alpha}{1} = \frac{\text{Observed Depression}}{\text{Normal Depression}} = \frac{2.44}{1.486}$$

$$\therefore \alpha = \frac{2.44}{1.486} - 1 = \frac{0.954}{1.486} = 0.642 \text{—i.e. } 64.2\% \text{ dissociated.}$$

Abnormal Results for Molecular Weights.

The relative lowering of vapour pressure, the elevation of the boiling point and the depression of the freezing point are each proportional to osmotic pressure, and hence, in normal cases, to the molecular concentration of the solute in the solvent.

Two types of abnormality have been noted and explained, in connection with osmotic pressure, on page 116. In one type the dissolved molecules are larger than normal, *i.e.* associated, in the other they are dissociated or ionised.

Thus alcohol, the molecular weight of which in water, as calculated from experimental observations of any of the above properties, is about 46, is found to give values up to 248 when dissolved in benzene. The value obtained increases as the concentration of the solution increases, and the highest value implies that a number of the alcohol molecules are then in aggregates of six simple molecules.

Similarly acetic acid, which is $\text{CH}_3\cdot\text{COOH}$ in water, appears to be mostly $(\text{CH}_3\cdot\text{COOH})_2$ when dissolved in benzene. This phenomenon is very common with compounds containing the $-\text{OH}$ group.

Confirmatory evidence of this explanation is found when partition coefficient measurements are made (see page 87).

Again, in the other type of abnormality due to dissociation the extent of the abnormality expressed as van 't Hoff's factor ' i ' depends on the concentration of the solution. This factor can be used to calculate the apparent degree of ionisation as in the examples above (page 117 and page 130). The values obtained show that the weaker a solution of an electrolyte the greater is the apparent degree of ionisation.

Further confirmation for these results is obtained quite independently from measurements of electrical conductivity of these solutions (see Chapter VIII).

QUESTIONS ON CHAPTER V.

Osmotic Pressure.

1. Write a brief account of some of the phenomena of osmotic pressure. Calculate the osmotic pressure of a 10% solution of cane-sugar (mol. wt. 342) at 15°C . (Camb. H.C.)

2. What is meant by the osmotic pressure of a solution and how is it measured?

State the laws of osmotic pressure for dilute solutions.

A solution contains 50 gm. of glycerol ($C_3H_8O_3$) per litre. Calculate its osmotic pressure in cm. of mercury at $17^\circ C$. (Lond. H.C.)

3. What is meant by 'the osmotic pressure' of a solution? Discuss the relation of this property to the molecular concentration and temperature of the solution. A solution of 42 gm. of mannitol in 1 litre of water was found to have an osmotic pressure of 5.55 atmospheres at $20^\circ C$. Calculate the molecular weight of the mannitol. (N.U.J.B., H.C.)

4. An aqueous solution of a non-electrolyte containing 4 gm. per 100 c.c. was found to have an osmotic pressure of 5.3 atmospheres at $15^\circ C$. What is its molecular weight? What are the practical objections to determining molecular weights by the direct measurement of osmotic pressure? (O. & C., H.C.)

5. What is the concentration of a solution in water of phenol, C_6H_5OH , which has an osmotic pressure of 0.324 atmosphere at $15^\circ C$?

6. Describe a method by which the osmotic pressure of a solution can be measured. To what extent is osmotic pressure analogous to gas pressure?

7. The mass of a substance which when volatilised occupied 10 litres at $97^\circ C$. and 740 mm. gave an osmotic pressure of 770 mm. when dissolved in 4.5 litres of water at $24^\circ C$. What conclusions do you draw from these facts? (Oxf. Schol.)

8. Discuss the analogy between gaseous pressure and osmotic pressure. Calculate the value of the constant R in litre atmospheres from the observation that a 1% solution of cane-sugar at $0^\circ C$. produces an osmotic pressure of 493 mm. of mercury.

Show that R has approximately the same value for gaseous pressure and for osmotic pressure. (Camb. Schol.)

9. Describe simple experiments which illustrate osmotic pressure. When the osmotic pressures of dilute equimolecular solutions of glucose $C_6H_{12}O_6$, and of sodium chloride are compared, it is found that the value of the osmotic pressure of the sodium chloride solution is 1.85 times as great as that of the glucose. Discuss this, showing how it is to be explained. (Camb., 1st M.B.)

10. If the osmotic pressure of a $\frac{N}{10}$ solution of potassium chloride at $18^\circ C$. is 4.44 atmospheres, calculate the apparent degree of ionisation.

11. A normal solution of potassium sulphate is 58% apparently ionised at $15^\circ C$.; calculate its osmotic pressure.

12. A solution of calcium chloride (2 gm.-mols. per litre) is found to be isotonic with one of glucose (4 gm.-mols. per litre). Calculate the apparent degree of ionisation of the calcium chloride.

Lowering of Vapour Pressure.

13. Explain briefly the relationship between the decrease of vapour pressure of a solvent and the molecular weight of the solute dissolved in this solvent. Describe an experimental method of measuring this lowering of vapour pressure.

14. The vapour pressure of water at 0°C . is 4.620 mm., while the vapour pressure of a solution of 88.9 gm. of a certain substance in 1000 gm. of water at the same temperature is 4.582 mm. Find the molecular weight of the substance. (Oxf. Schol.)

15. The vapour pressure of ether, $\text{C}_4\text{H}_{10}\text{O}$, at 10°C . is 292 mm. A solution, also at 10°C ., containing 10.6 gm. of benzaldehyde in 100 gm. of ether has a vapour pressure of 272 mm. What is the molecular weight of benzaldehyde?

16. A current of dry air is passed through a solution containing 5 gm. phenol in 50 gm. of water, and then through pure water. If the loss in weight of the former is 1.85 gm. and of the latter is 0.036 gm., calculate the molecular weight of phenol.

17. How may the molecular weight of a substance be determined by the method of the lowering of the vapour pressure?

Calculate the molecular weight of a substance a solution of which containing 7.08 gm. dissolved in 100 gm. of water has a vapour pressure at 0°C . of 4.557 mm., that of water being 4.620 mm. What would be the osmotic pressure of the solution? (Camb. Schol.)

18. The vapour pressure of a 3% solution of sodium chloride at 15°C . is 12.5 mm., and that of pure water at this temperature is 12.7 mm. Calculate the apparent degree of ionisation of the sodium chloride.

19. The osmotic pressure of a decinormal solution of potassium chloride is 4.46 atmospheres at 20°C . The vapour pressure of pure water at 20°C . is 17.5 mm. Calculate the vapour pressure of the solution. (Camb. Schol.)

Elevation of Boiling Point.

20. How may the molecular weight be determined by the method of elevation of the boiling point?

The boiling point of pure acetone is 56.38°C . at normal barometric pressure. A solution of 0.707 gm. of a compound in 10 gm. of acetone boiled at 56.88°C . What is the molecular weight of the compound if the molecular elevation constant for acetone per 100 gm. is 16.7°C .? (Camb. Schol.)

21. A 2% solution of nicotine in water boils at 100.062°C . Calculate the molecular weight of nicotine.

22. Describe an accurate method of measuring the change in the boiling point of a liquid brought about by the addition of a soluble solid.

What conditions must be fulfilled if this change is to be utilised to find the molecular weight of the dissolved solid?

The boiling point of an aqueous solution containing 19.54 gm. per litre of an organic compound is found to be 100.11°C . What is the molecular weight of the compound? (The latent heat of vaporisation of water is 537.) (Oxf. Schol.)

23. An aqueous solution of an acid so weak as to be practically unionised in the given solution boiled at 100.40°C . and 25 c.c. of the solution required 38.5 c.c. of normal soda for neutralisation. The boiling-point constant for water is 5.20. Determine the basicity of the acid. (Camb. Schol.)

24. The molecular elevation constant per 100 gm. for carbon disulphide is 29.6°C . A solution of 2.58 gm. benzoic acid dissolved in 50.1 gm. carbon disulphide boiled at 0.48°C . above the boiling point of pure carbon disulphide. What conclusion can you draw as to the molecular condition of the benzoic acid?

25. A solution of calcium chloride in water contains 4.8 gm. per litre and boils at 100.057°C . under normal atmospheric pressure. Calculate the apparent degree of ionisation of the calcium chloride.

Depression of Freezing Point.

26. If you were provided with apparatus for finding the freezing points of aqueous solutions, a freely-soluble non-electrolyte with molecular weight 60 and a specimen of a substance *X* also soluble in water, describe and explain how you would proceed to find the molecular weight of *X*. (Camb. 1st. M.B.)

27. Explain how the molecular weight of a substance may be determined from observations of the depression of the freezing point.

If 1 gm. of a substance is dissolved in 15 gm. of water the freezing point is lowered 0.37°C . What is the molecular weight of the dissolved substance? The constant for water is 18°C . (Camb. H.C.)

28. A solution containing 0.50 gm. of acetone in 100 gm. of glacial acetic acid gives a depression of the freezing point of the acetic acid of 0.34°C . If the molecular depression constant for glacial acetic acid per 100 gm. is 39°C ., calculate the molecular weight of acetone.

29. Camphor melts at 175°C . An intimate mixture of 2.0 gm. of camphor with 0.100 gm. of naphthalene (C_{10}H_8) melts at 160°C . Also a mixture of 2.0 gm. of camphor with 0.100 gm. of a substance *X* melts at 165°C . Calculate the molecular weight of *X*.

What advantages do you consider the method indicated above to have over the Beckmann freezing-point method of determining molecular weights? Describe briefly how you would conduct the determination. (C.W.B., H.C.)

30. 0.50 gm. of *m*-dinitrobenzene, $\text{C}_6\text{H}_4(\text{NO}_2)_2$, when dissolved in 50 gm. of nitrobenzene lowered the freezing point of the latter by 0.417°C . What value do these figures give for the molecular depression constant of nitrobenzene?

31. Describe, with experimental details, how the molecular weight

of a dissolved substance may be found from the depression of the freezing point of a solvent.

Two solutions containing, respectively, 7.5 gm. of urea (CON_2H_4) and 42.75 gm. of a substance X in 1000 gm. of water, freeze at the same temperature. Calculate the molecular weight of X . (Lond. H.C.)

32. The freezing point of pure benzene is 5.50°C . A solution containing 2.5 gm. of benzoic acid ($\text{C}_6\text{H}_5\cdot\text{COOH}$) in 72 gm. of benzene freezes at 4.79°C . Explain the result which these figures give for the molecular weight of benzoic acid in benzene. (k for benzene = 51°C . per 100 gm.)

33. Calculate the molecular weight of acetanilide ($\text{C}_8\text{H}_9\text{ON}$) from the following data and comment on the results :

1.45 gm. acetanilide in 100 gm. benzene caused a freezing-point depression of 0.464°C . In a second experiment 7.52 gm. of acetanilide in 100 gm. benzene caused a freezing-point depression of 1.45°C . (k for benzene = 51.2°C . per 100 gm.) (Camb. H.C.)

34. Explain how the molecular weight of a substance may be deduced from measurements of the freezing point of its solution. Draw deductions from the following data : a weight-normal (1 gm. molecular weight in 1000 gm. of water) solution of acetic acid freezes at -1.865°C ., and of hydrochloric acid at -3.352°C . (k constant for water = 18.57°C .) (Camb. Schol.)

35. The freezing-point of nitrobenzene is 3°C . A solution of 1.20 gm. of chloroform in 100 gm. of nitrobenzene freezes at 2.3°C . A solution of 0.6 gm. of acetic acid in 100 gm. of nitrobenzene freezes at 2.64°C . From these data make what deductions you can concerning the molecular state of acetic acid when dissolved in nitrobenzene. (Camb. Schol.)

36. A normal solution of sodium nitrate has an apparent degree of ionisation of 63%. What will its freezing point be? (k for water = 18.6°C .)

37. A solution containing 8 gm. of zinc nitrate, $\text{Zn}(\text{NO}_3)_2$, per litre of water freezes at -0.20°C . Calculate the apparent degree of ionisation of the zinc nitrate in this solution. (k for water = 18.6°C .)

38. The freezing point of a $0.75 \frac{N}{100}$ KOH solution is -0.0275°C . What is the concentration of OH ions in this solution? (k for water = 18.6°C .)

39. Solutions of $\frac{1}{10}$ molar concentration of the following substances in benzene have the freezing points stated below :

Methyl iodide 4.90°C ., naphthalene 4.90°C ., nitrobenzene 4.92°C ., phenol 5.08°C ., ethyl alcohol 5.12°C ., methyl alcohol 5.15°C ., acetic acid 5.15°C .

The freezing point of benzene is 5.40° . State what conclusions may be drawn from these data. What further evidence or experiments can you suggest to confirm these conclusions? (Camb. Schol.)

40. A metallic chloride X , containing 26.2% of chlorine, boiled at

303°C. , and its vapour density at this temperature was 140; at 600°C. the vapour density was 138. When 1 gm. of X was dissolved in 100 gm. of water, the freezing point of the solution was -0.056°C. A similar solution of 1 gm. of potassium chloride froze at -0.446°C.

What conclusions about X can you draw from these data? Indicate the experiments you would make to confirm your conclusions. ($k = 18.6^{\circ}\text{C.}$, $\text{Cl} = 35.5$.) (Camb. Schol.)

Depression and Elevation Constants and Latent Heat.

41. The melting point of naphthalene is 80°C. and its latent heat of fusion is 35.7 cal. per gm. Calculate the molecular depression constant.

42. The freezing point of glacial acetic acid is 17°C. and its molecular depression constant per 100 gm. is 39°C. What value do these figures give for the latent heat of fusion of acetic acid?

43. A solution containing 0.97 gm. camphor, of molecular weight 152, in 21.390 gm. of acetone was found to boil at 56.8°C. If the boiling point of pure acetone is 56.3°C. , calculate the latent heat of vaporisation of acetone.

CHAPTER VI

LAW OF MASS ACTION

Factors Affecting Chemical Change.

A CHEMICAL equation as ordinarily written gives no indication of the ease or the rate with which the reaction will proceed, nor of the physical conditions necessary to give a desired result. Such knowledge is often vitally important in the laboratory and in industrial processes.

The effect of *temperature* is often quite obvious, but the explanation of this effect depends on a knowledge of the thermochemistry of reactions (see Chapter VII).

The phenomena of *catalysis* are also very important, and will be studied in Chapter IX.

The quantitative effect of the *concentrations* of the reacting substances, which in the case of gases correspond with *pressures*, was studied by Guldberg and Waage (1864), who enunciated the following law :

LAW OF MASS ACTION.

The rate at which a chemical reaction proceeds is proportional to the 'active masses' (usually molecular concentrations) of the reacting substances.

If the reaction is reversible, then as new substances are produced and the concentrations of the original substances are reduced, the rate of the backward reaction will increase and the rate of the forward reaction will diminish until an *equilibrium position* is reached.

The Law of Mass Action is easily derived from a kinetic view of matter, for, if the assumption is made that for reaction to occur, collision between the reacting molecules must take place, it follows that the rate of reaction will be proportional to the number of collisions. Further, the number of collisions will be proportional to the concentrations of the reacting molecules.

In homogeneous systems, in which every molecule has an equal chance of reacting with any other molecule, the active mass is normally (see activity factor, page 156) measured by the number of molecules per unit volume (usually gram molecules per litre).

It will be seen, in examples given later, that the "active mass" must sometimes be represented by the square, cube, or even higher power of the molecular concentration.

In heterogeneous systems this will not apply. For example, in the case of the reaction between a gas and a solid, only the surface molecules of the latter can react. Their concentration will not depend, therefore, on the pressure, nor on the weight of solid within the surface but, for a given temperature, it will remain constant.

The rate of reaction means the velocity with which the molecular concentrations of the reacting substances are changing.

Thus if a substance consisting of a gram-molecules per unit volume decomposes so that, after a time t_1 seconds, x_1 gram-molecules per unit volume have changed, then $a - x_1$ gram-molecules per unit volume will remain unchanged. After t_2 secs. if x_2 have decomposed, $a - x_2$ will remain. The concentration of the substance is gradually diminishing and the rate of change will also diminish. During the interval $(t_2 - t_1)$ secs., the average value of the concentration of the unchanged substance is $\frac{(a - x_1) + (a - x_2)}{2} = a - \frac{x_1 + x_2}{2}$ gram-molecules per unit volume, and the average rate of change is $\frac{(a - x_1) - (a - x_2)}{t_2 - t_1} = \frac{x_2 - x_1}{t_2 - t_1}$ gram-molecules per unit volume per second.

The Law of Mass Action states that $\frac{x_2 - x_1}{t_2 - t_1} = k \left(a - \frac{x_1 + x_2}{2} \right)$, where the differences $x_2 - x_1$ and $t_2 - t_1$ are very small. When these differences are infinitesimally small, this average rate becomes the actual rate at time t ($t_1 = t_2 = t$), when x ($x_1 = x_2 = x$) gram-molecules per unit volume have changed. The above expression for the rate then becomes equal to $k(a - x)$ or in the notation of the calculus

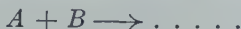
$$\frac{dx}{dt} = k(a - x)$$

If a substance X is in process of transformation into another substance Y , and if at any moment the active mass of X is represented by C (usually expressed in gram-molecules per litre), then we have:



and the rate of reaction *at this moment* $= k \times C$, where k is called the **velocity constant**. k varies with the temperature and with the nature of the reacting substance.

If two substances A and B are reacting, and if their active masses at *any particular moment* are C_A and C_B then :



and *at this moment* rate of reaction $= k \times C_A \times C_B$.

Active masses of substances are often written $[A]$, $[B]$, instead of C_A , C_B .

In certain decompositions the equation is of the form :



e.g.



Such a reaction can only occur when one molecule of A meets another molecule of A and the reaction is of the type



The student must be careful not to press this analogy with $A + B \longrightarrow \dots$ too closely, or he will be tempted to write the active mass of A , say C_A , as two equal parts $\frac{1}{2}C_A$ and $\frac{1}{2}C_A$, and hence obtain the rate of reaction as equal to $k \times \frac{1}{2}C_A \times \frac{1}{2}C_A$.

This is not true, for whereas in the reaction $A + B \longrightarrow$ a molecule of A can only react with a molecule of B , in the reaction $A + A \longrightarrow \dots$ half the molecules of A can react with the other half, but they can also react with each other.

The rate of the reaction $2A \longrightarrow \dots$ if C_A is the active mass of A is equal to $k \times C_A^2$.

Order of Reaction.

Reactions of the First Order.

These reactions are of the type $X \longrightarrow Y$ in which rate $= k \times C$ (see above).

It must be remembered that C is the active mass of X at the moment when the rate is being considered.

If, however, a represents the number of molecules of X before the reaction commences, and if x is the number which have changed into Y after a time t , then $(a - x)$ molecules remain, and the rate of change at this time is

$$\frac{dx}{dt} = k(a - x)$$

By integration we have :

$$t = \int \frac{dx}{k(a-x)} = -\frac{1}{k} \log_e (a-x) + \text{constant } c.$$

If $x = 0$ when $t = 0$, then $0 = -\frac{1}{k} \log_e a + c$ and

$$\therefore c = \frac{1}{k} \log_e a$$

Finally, $t = -\frac{1}{k} \log_e (a-x) + \frac{1}{k} \log_e a = \frac{1}{k} \log_e \frac{a}{(a-x)}$

or $k = \frac{1}{t} \log_e \frac{a}{a-x}$

$$= \frac{1}{t} \log_{10} \frac{a}{a-x} \times \log_e 10 = \frac{2.3}{t} \log_{10} \frac{a}{a-x}.$$

It is interesting to note that in this equation if $x = \frac{1}{2}a$ or any other fraction of a , then $t = \frac{2.3}{k} \log_{10} \frac{a}{a-\frac{1}{2}a}$, etc., $= \frac{2.3}{k} \log_{10} 2$.

Therefore in a unimolecular reaction, or reaction of the first order, the time taken for any definite fraction of the reaction to be completed is independent of the initial concentration.

The decomposition of various organic compounds such as acetone are found to be unimolecular, but in general truly unimolecular reactions are very rare. The decomposition of nitrogen pentoxide, N_2O_5 , is almost the only case in inorganic chemistry, and this may be $\text{N}_2\text{O}_5 \longrightarrow \text{N}_2\text{O}_4 + \text{O}$ and $\text{O} + \text{O} \longrightarrow \text{O}_2$ (instantaneous).

Other reactions, which from the equation would appear to be of a higher order, often obey the unimolecular law, since they occur in stages. Of these stages one may be unimolecular and relatively slow and it is this slow reaction which determines the rate of the complete reaction. For example, the catalytic decomposition of hydrogen peroxide takes place in two stages : $\text{H}_2\text{O}_2 \longrightarrow \text{H}_2\text{O} + \text{O}$ and $\text{O} + \text{O} \longrightarrow \text{O}_2$, the second being instantaneous.

This decomposition is catalysed by such substances as platinum black, and the rate of reaction may be measured either by collecting the oxygen evolved or by titrating, at measured intervals, specimens of the unchanged hydrogen peroxide by means of standard potassium permanganate.

Similarly the unimolecular law is obeyed when a gas such as

PH_3 decomposes. The decomposition occurs on the surface of the containing vessel, and the number of molecules reaching the surface in a given time will be proportional to the pressure. This determines the order of the reaction regardless of the order of the rapid reaction which occurs at the surface of the container.

Further reactions, such as the inversion of cane-sugar (see page 144) are unimolecular, for since as in this case the amount of water compared with that of the sugar is so large that its active mass may be regarded as constant.

A similar argument applies in the case where the concentration of one of the reactants is kept constant artificially. For example, in an experiment devised by Harcourt and Esson, hydrogen peroxide reacts with acidified potassium iodide thus :

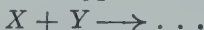


If sodium thiosulphate is added just as fast as the iodine is formed (as indicated by starch solution), then sodium iodide is produced, and with free acid present this maintains the concentration of hydrogen iodide at a constant value.

The reaction, as measured by the rate of addition of the sodium thiosulphate, is then unimolecular.

Reactions of the Second Order.

These are reactions of the type :



If a and b represent the number of molecules of X and Y before the reaction starts, and if x molecules of X , and therefore x molecules of Y , react after time t then :

$$\text{Rate of reaction is } \frac{dx}{dt} = k(a-x)(b-x)$$

$$\text{Integration gives } k = \frac{1}{t(a-b)} \log_e \frac{b(a-x)}{a(b-x)}$$

In the special cases when equimolecular amounts of X and Y are used, and also when the reaction is of the type $2A \longrightarrow \dots$

$$\text{the rate of reaction is } \frac{dx}{dt} = k(a-x)^2$$

$$\therefore = \int \frac{dx}{k(a-x)^2} = \frac{1}{k} \times \frac{1}{a-x} + \text{integration constant } c.$$

If $x = 0$ when $t = 0$, then $0 = \left(\frac{1}{k} \times \frac{1}{a}\right) + c$ and $\therefore c = -\frac{1}{ka}$

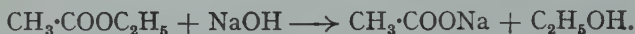
$$\therefore t = \frac{1}{k} \left(\frac{1}{a-x} \right) - \frac{1}{ka} = \frac{1}{k} \frac{x}{a(a-x)}$$

$$\therefore k = \frac{1}{t} \frac{x}{a(a-x)}$$

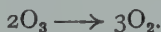
From this result, it will be noticed that for the change to be half completed—i.e. for $x = \frac{1}{2}a$ —the time $t = \frac{1}{k} \times \frac{1}{a}$. Thus in a bimolecular reaction the time for a fraction of the reaction to occur is *not* independent of a , the concentration.

Typical reactions of the second order are :

(1) The hydrolysis of an ester such as ethyl acetate by means of caustic soda



(2) The decomposition of ozone



Reactions of the Third Order.

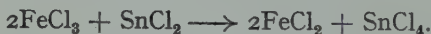
If the initial concentrations of the reacting substances are equal to a , then we have rate of reaction :

$$\frac{dx}{dt} = k(a-x)^3$$

Integration gives

$$k = \frac{1}{2t} \left(\frac{1}{(a-x)^2} - \frac{1}{a^2} \right)$$

A reaction which agrees approximately with this is the reduction of ferric chloride solution by stannous chloride



This reaction was investigated by Noyes and Brann. Equivalent solutions of ferric chloride and stannous chloride were mixed in a thermostat. After fixed intervals of time, small measured volumes of the mixture were removed and run into mercuric chloride solution to remove unchanged stannous chloride. The remaining ferrous salt was then determined by titration with potassium dichromate.

Reactions of the fourth, fifth and higher orders are rarely found. This is probably due to the fact that the reactions take place in stages and the slowest determines the rate which is finally measured.

Determination of the Order of a Reaction.

(1) Suitable observations are made to determine the concentrations of the reacting substances after known intervals of time.

By substitution of these results in the formulæ for k given above the formula which gives the best constant can be found.

(2) The time required for a definite fraction—say one-half—of the reaction to reach completion is measured.

For a unimolecular reaction this time is independent of the initial concentration, while for a bimolecular reaction it is inversely proportional to the initial concentration (see above).

In general, if a_1 and a_2 are two values for the initial concentration, and if t_1 and t_2 are the times taken, respectively, for the reaction to be half completed, then :

$$\frac{t_2}{t_1} = \left(\frac{a_1}{a_2}\right)^{n-1}, \text{ where } n \text{ is the order of the reaction.}$$

Practical Illustration of Reaction Velocity.

A simple practical illustration of the effect of concentration on rate of reaction may be seen in the reaction between hydrochloric acid and sodium thiosulphate.



Five small beakers containing respectively, 0.1 gm., 0.2 gm., 0.3 gm., 0.5 gm., and 1.0 gm. of 'hypo' crystals per 100 c.c. of water are placed in a row on a sheet of black paper.

Five boiling tubes containing dilute hydrochloric acid (1 c.c. conc. HCl to 20 c.c. water) are mounted in holes on a wooden lath so that when tilted the tubes will deliver their contents into the beakers simultaneously. The time is noted by a stop clock.

As the reaction proceeds colloidal sulphur is produced and the times are recorded for the contents of the beakers to reach the same degree of milkyiness.

It will be found that these times are approximately inversely proportional to the quantities of hypo originally in the beakers.

The advanced student will find the following theoretical deduction of interest :

The concentration of hydrochloric acid is large and may be assumed to be constant, and therefore the reaction may be regarded as of the first order.

x = concentration of sulphur necessary to make the solution appear distinctly turbid.

a = original concentration of hypo.

x is the same in each experiment and is therefore a constant in the expression :

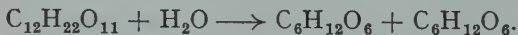
$$\begin{aligned} k &= \frac{1}{t} \log_e \frac{a}{a-x} = \frac{1}{t} \log_e \left(1 + \frac{x}{a-x} \right) \\ &= \frac{1}{t} \log_e \left(1 + \frac{x}{a} \right), \quad x \text{ being small compared with } a. \\ &= \frac{1}{t} \left(\frac{x}{a} - \frac{x^2}{2a^2} + \frac{x^3}{3a^3} \dots \right) \\ &= \frac{1}{t} \times \frac{x}{a} \text{ since } \frac{x^2}{a^2}, \frac{x^3}{a^3} \text{ are very small.} \end{aligned}$$

$$\therefore a \times t = \frac{x}{k}, \text{ which is constant.}$$

Experimental Verification of the Law of Mass Action (Dynamic Method).

(a) The Inversion of Cane-Sugar.

A solution of cane-sugar in water exhibits optical activity, that is, it rotates the plane of polarisation when polarised light is passed through it. There is a slow chemical action between the water and the sugar producing equimolecular quantities of glucose and fructose. The reaction may be accelerated by adding dilute acid as a catalyst



Glucose and fructose are both optically active, but fructose rotates the plane of polarisation of the light to the left and glucose to the right. Cane-sugar is itself dextrorotatory. Moreover, the laevorotatory power of fructose per molecule is larger than that of glucose, so that the rotation diminishes as the reaction proceeds and is eventually to the left and hence 'inverted.'

The rate of the reaction can therefore be observed by measurement of the rotation effect on a beam of light in a polarimeter.

A solution of cane-sugar (15 to 20 gm. per 100 c.c.) mixed with an equal volume of normal hydrochloric acid is placed in the polarimeter tube which must be kept at a constant temperature by means of a water-jacket.

Polarimeter readings should be taken every half-minute during the early stages, and then at longer intervals, and a final reading should be taken after 48 hours, by which time the change will be complete.

Results.

Method (1). If A_0 , A_t , A_∞ , are the polarimeter readings at the start, after time t , and at the end, respectively, then $A_0 - A_\infty$ is proportional to the original concentration of the cane-sugar and $A_t - A_\infty$ is proportional to the concentration after time t . These angles of rotation must of course be given their correct + and - signs.

The values for A_0 , A_∞ , and A_t for the corresponding values of t can be substituted in the expression :

$$k = \frac{2.3}{t} \log_{10} \frac{A_0 - A_\infty}{A_t - A_\infty}$$

A constant value is then obtained for k , showing that the Law of Mass Action applies to this reaction. Since, as explained previously, the water is in such excess that its concentration is practically constant, and since the hydrochloric acid is only a catalyst, the reaction is unimolecular.

The above expression is easily proved :

If $a - x$, x , x are the number of molecules of cane sugar, glucose and fructose present after time t and α , β , γ are the molecular rotations of these substances respectively, then

$$A_t = (a - x)\alpha + x\beta - x\gamma$$

$$A_0 = a\alpha$$

$$A_\infty = a\beta - a\gamma$$

$$\begin{aligned} \frac{A_0 - A_\infty}{A_t - A_\infty} &= \frac{a(\alpha - \beta + \gamma)}{(a - x)\alpha + (x - a)\beta - (x - a)\gamma} \\ &= \frac{a}{a - x}. \end{aligned}$$

Method (2). A curve showing the relation between concentration of cane-sugar and time can be plotted as in Fig. 50a.

If A and B are two points on this curve, then AC represents the change in concentration in time BC and $\frac{AC}{BC}$ represents the average rate of change during this interval. If these two points are taken very close together, we obtain a tangent to the curve at a point—say P —and the slope of this tangent which is $\frac{PQ}{QR}$ or $\tan \theta$ represents the rate of change at the moment when the concentration of cane-sugar is PQ .

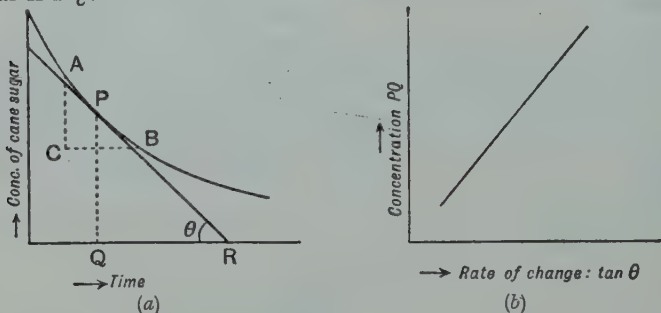
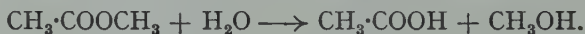


FIG. 50.

Several such tangents may be drawn. If the corresponding values of $\tan \theta$ and PQ are plotted against each other, a second curve (Fig. 50*b*) is obtained. This is found to be a straight line, showing that the rate of change of the concentration is proportional to the concentration, thus verifying the unimolecular law.

(b) *Hydrolysis of Methyl Acetate.*

As in the previous example, this hydrolysis, with excess of water and with dilute acid as a catalyst, is unimolecular



The rate of reaction can be measured by titrating the acetic acid produced. 20 c.c. of $\frac{N}{2}$ -HCl are contained in a flask, immersed in a thermostat at 20° C. or 25° C., and about 1 c.c. of pure methyl acetate is added and the mixture is well shaken.

2 c.c. of the mixture are withdrawn and transferred to a flask containing 20 c.c. or 30 c.c. of water (free from carbon dioxide). This will almost stop the reaction, and the resulting solution is then

titrated as quickly as possible with $\frac{N}{20}$ -NaOH. The time corresponding to this titration reading will be taken when the 2 c.c. of mixture have been added to the water. A series of readings, and a final reading when reaction is complete, are taken at measured intervals of time, 10, 20, 30 minutes, etc.

If T_1, T_2, T_∞ are titration readings at times t_1, t_2, t_∞ , then :

$$k = \frac{2.3}{t_2 - t_1} \log_{10} \frac{T_\infty - T_1}{T_\infty - T_2}$$

N.B.—Some NaOH will be required to neutralise HCl, but this amount will be constant and will not affect the differences $T_\infty - T_1, T_\infty - T_2$.

In reactions of this type the acceleration of the rate of reaction due to the catalyst is usually regarded as being proportional to the hydrogen-ion concentration provided by the acid (but, see page 202).

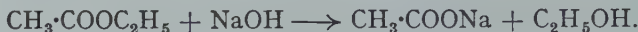
Hence if the experiment is repeated with $\frac{N}{2}$ -H₂SO₄ instead of the $\frac{N}{2}$ -HCl, the ratio of the constants obtained will give the relative 'strengths' of the two acids. (See also Strengths of Acids, page 201.)

(c) *Saponification of an Ester, e.g. Ethyl Acetate.*

60 c.c. of equimolecular solutions $\left(\frac{N}{20}\right)$ of ethyl acetate and sodium hydroxide are placed in a thermostat. After these solutions have had time to reach a constant temperature, 50 c.c. of each solution are mixed in another flask, also in the thermostat. The time of starting the reaction is taken as that when half of one solution has been added to the other.

After intervals of three minutes 10 c.c. portions of the reacting mixture are withdrawn and transferred rapidly to small flasks containing 10 c.c. of $\frac{N}{20}$ nitric acid. This neutralises any unchanged sodium hydroxide and stops the reaction. The excess of nitric acid in each flask is then determined by titration with $\frac{N}{20}$ sodium hydroxide.

The amount of sodium hydroxide (x) which has been used up in the hydrolysis of the ester after time t represents an equimolecular quantity of ethyl acetate. The amount remaining is $(a - x)$, where a is the initial 'titration value' of the sodium hydroxide



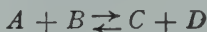
This reaction is bimolecular and the titration readings are found to agree with the expression :

$$k = \frac{1}{t} \frac{x}{a(a-x)}$$

The actual value of k will obviously depend on the units in which a , x and t are expressed.

Law of Mass Action and Reversible Reactions.

Let us consider a reaction of the type



As the reaction proceeds the active masses of the original substances A and B diminish and the rate of the forward reaction gradually decreases. At the same time substances C and D are being produced in increasing quantities. The rate at which they react to form A and B therefore gradually increases. Eventually equilibrium is reached when the forward rate is equal to the rate of the backward reaction.

If C_a , C_b , C_c , C_d , represent the *concentrations in the equilibrium position*,

then : Rate of forward reaction = $k_1 \times C_a \times C_b$, where k_1 is the velocity constant

and Rate of backward reaction = $k_2 \times C_c \times C_d$, where k_2 is the velocity constant.

$$\therefore k_1 \times C_a \times C_b = k_2 \times C_c \times C_d$$

$$\therefore \frac{C_c \times C_d}{C_a \times C_b} = \frac{k_1}{k_2} = K$$

K is independent of the initial concentrations and only depends on temperature. It is called the *Equilibrium Constant*. For the effect of temperature on the equilibrium constant see page 170.

If a and b are the initial molecular concentrations of A and B , those of C and D being nil, and if x molecules per unit volume are changed after time t , then, at this instant, we have

$$C_a = a - x, C_b = b - x, C_c = C_d = x.$$

Hence rate of forward reaction $= k_1 \times (a - x) \times (b - x)$
and rate of backward reaction $= k_2 \times x \times x$

The nett rate of the reaction from left to right, at time t , is therefore

$$\frac{dx}{dt} = k_1(a - x)(b - x) - k_2x^2$$

The integration of this equation is beyond the scope of this book and k_1 and k_2 can only be calculated if $K = \frac{k_1}{k_2}$ is also determined from measurements when equilibrium is reached.

If, however, the concentrations $a - x$, $b - x$, and x are those when equilibrium is reached, then :

$$\frac{x^2}{(a - x)(b - x)} = K$$

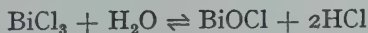
or if there are initially equimolecular quantities of A and B , then $a = b$ and we have :

$$\frac{x^2}{(a - x)^2} = K.$$

N.B.—It is important to note that it is customary, in working out an equilibrium constant, to insert the concentrations of the substances produced as numerator and those of the original reactants as denominator.

Practical Illustrations of Reversible Reactions.

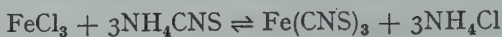
A simple reversible reaction is that between bismuth chloride and water giving hydrochloric acid and a white precipitate of bismuth oxychloride.



On the addition of hydrochloric acid the equilibrium is displaced from right to left and the solution becomes clear. With excess of

water the equilibrium is moved in the opposite direction and the white precipitate reappears.

Another example is afforded by the reversible reaction between ferric chloride and ammonium thiocyanate solutions



The presence of ferric thiocyanate is shown by its blood-red colour. It is interesting to mix various proportions of $\frac{N}{10}$ solutions of these two salts (e.g. 10 c.c. : 10 c.c.; 10 c.c. : 20 c.c., etc.) in 100 c.c. measuring cylinders. In each case distilled water is added to the mixture to give a constant total volume of 100 c.c. The tint of the blood-red colour gives an indication of the equilibrium position.

Applying the Law of Mass Action to this reaction we obtain the expression

$$\frac{[\text{Fe}(\text{CNS})_3] \times [\text{NH}_4\text{Cl}]^3}{[\text{FeCl}_3] \times [\text{NH}_4\text{CNS}]^3} = K$$

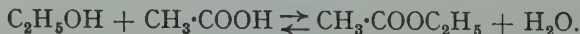
The terms $[\text{FeCl}_3]$, etc., represent molecular concentrations of the salts in the *equilibrium position*.

Since in the above equation the concentration of the ammonium thiocyanate is cubed it follows that, if the quantities of ferric chloride and ammonium thiocyanate mixed together are as 1 : 2, then the reaction will proceed further before reaching equilibrium than if the proportion is as 2 : 1.

This is verified by the deeper tint obtained in the former case.

Experimental Verification of the Law of Mass Action (Static Method).

Ethyl alcohol and acetic acid react to form an ester, ethyl acetate, and water and this is a reversible reaction



Different proportions of absolute ethyl alcohol and glacial acetic acid (1 gm. : 1 gm.; 2 gm. : 1 gm., etc.) are placed in sealed tubes and heated in a water-bath at 50° C. for several hours. The tubes are allowed to cool and the contents are washed out with water and titrated with standard caustic soda (indicator—phenol

phthalein). Titration results give the amount of acetic acid present in the equilibrium position, for since the reaction is very slow the equilibrium does not change during the titration. From this, the amount of acid changed is obtained and from the equation we know that an equimolecular amount of alcohol must have disappeared, producing equimolecular quantities of ethyl acetate and of water.

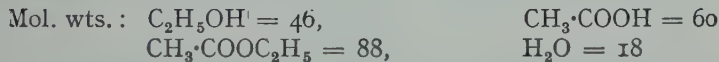
In the equilibrium position it is found that

$$\frac{[\text{molecular conc. of ester}] \times [\text{mol. conc. of water}]}{[\text{mol. conc. of alcohol}] \times [\text{mol. conc. of acid}]} = K.$$

If the Law of Mass Action is obeyed then, for a given temperature, the same value for K is obtained no matter what quantities of alcohol and acid are used initially. In this particular reaction the value of K only varies very slightly with the temperature and is equal to 4.

Example.

60 gm. of acetic acid were heated with 46 gm. of ethyl alcohol at 50° C. until equilibrium was established. 12 gm. of water and 58.7 gm. of ethyl acetate were produced. What quantities of these substances would be obtained if 90 gm. of acetic acid and 92 gm. of alcohol were heated to the same temperature?



Hence 60 gm. acetic acid = 1 gm.-mol.; 46 gm. ethyl alcohol = 1 gm.-mol.

12 gm. water = $\frac{12}{18} = \frac{2}{3}$ gm.-mol.; 58.7 gm. ethyl acetate = $\frac{58.7}{88} = \frac{2}{3}$ gm.-mol.

Hence $\frac{2}{3}$ gm.-mol. of acetic acid and of the alcohol must have disappeared in order to produce $\frac{2}{3}$ gm.-mol. of water and of ethyl acetate, leaving $\frac{1}{3}$ gm.-mol. of each unchanged.

In the equilibrium position

$$K = \frac{\frac{2}{3} \times \frac{2}{3}}{\frac{1}{3} \times \frac{1}{3}} = 4.$$

In the second experiment if x gm.-mols. of water and of ester are produced, then

$$K = \frac{x \times x}{(1\frac{1}{2} - x)(2 - x)} = 4$$

$$\therefore \frac{x^2}{4} = 3 - 3\frac{1}{2}x + x^2 \quad \therefore 3x^2 - 14x + 12 = 0$$

$$\therefore x = \frac{14 \pm \sqrt{196 - 144}}{6} = \frac{7 \pm \sqrt{13}}{3} = \frac{7 \pm 3.61}{3} = 3.54 \text{ or } 1.13.$$

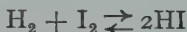
Of these values the former is inadmissible, since if all the acetic acid is transformed, the number of molecules of ethyl acetate produced can only be $1\frac{1}{2}$.

Hence the equilibrium mixture will contain 1.13 gm.-mols. water $= 1.13 \times 18 = 20.34$ gm., and 1.13 gm.-mols. ester $= 1.13 \times 88 = 99.44$ gm.

The Equilibrium between Hydrogen, Iodine, and Hydrogen Iodide.

This equilibrium was investigated by Bodenstein. Various proportions of hydrogen and iodine were heated in sealed tubes to 450°C . After rapid cooling the contents of the tubes were analysed.

The cooling must be as rapid as possible in order to 'freeze' the equilibrium, *i.e.* the equilibrium must not have time to adjust itself to the new conditions.



If a gm.-mols. and b gm.-mols. in volume V represent the initial concentrations of hydrogen and iodine respectively, and if when equilibrium is reached x gm.-mols. of each have combined together then $2x$ gm.-mols. of hydrogen iodide have been produced.

$$\therefore \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right)\left(\frac{b-x}{V}\right)} = K$$

$$\text{or } \frac{4x^2}{(a-x)(b-x)} = K.$$

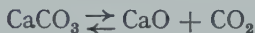
Thus when the Law of Mass Action is applied to this type of reaction, in which there is no volume change, V cancels out and does not occur in the expression for K .

The Law of Mass Action and Heterogeneous Reactions.

The Law of Mass Action can only be applied strictly to a single phase in which the molecules are uniformly distributed so that they all have an equal chance of reacting (see page 138).

In the case of a system which is heterogenous—for example, one consisting of solids and a vapour, or one consisting of solids and a liquid—we can apply the law to the equilibrium in one phase. Such cases are the decomposition of calcium carbonate (see below), and the ionic equilibrium in a saturated solution in contact with a solid (see page 194).

The Dissociation of Calcium Carbonate.



It is simplest to consider the reaction taking place, in the vapour phase, between carbon dioxide and the vapours of calcium carbonate and calcium oxide. The concentrations are proportional to the partial pressures of the vapours, and if in the equilibrium position these are P_{CO_2} , P_{CaCO_3} , and P_{CaO} we have (see page 155) :

$$\frac{P_{\text{CO}_2} \times P_{\text{CaO}}}{P_{\text{CaCO}_3}} = Kp.$$

For a given temperature the vapour pressures of calcium carbonate and calcium oxide in contact with the solids are constant and hence

$$P_{\text{CO}_2} = k.$$

Thus in a closed vessel the carbon dioxide has a fixed '*dissociation pressure*' for a given temperature. This result is also predicted by the Phase Rule (see page 104). The fact that in a reaction of this type the dissociation pressure does not depend on the amount of solid, but only on the temperature, is sometimes known as *Deville's Law*.

The Action of Steam on Red-hot Iron.



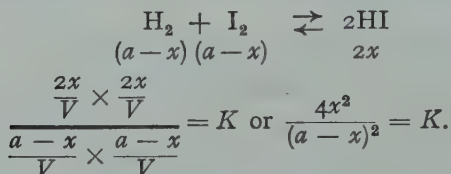
Applying the Law of Mass Action to the vapour phase, we have :

$$\frac{P_{\text{Fe}_3\text{O}_4} \times (P_{\text{H}_2})^4}{(P_{\text{Fe}})^3 \times (P_{\text{H}_2\text{O}})^4} = K \quad \therefore \quad \frac{P_{\text{H}_2}}{P_{\text{H}_2\text{O}}} = k.$$

Hence if P_{H_2O} is increased by passing more steam over the iron, then P_{H_2} is also increased and the equilibrium moves from left to right, and vice versa.

Reactions Involving Volume Changes.

In the reactions so far considered, the effect of changes of volume has not been dealt with. Molecular quantities rather than molecular concentrations are often written in the equilibrium equation, for in cases where there is no volume change the volume will cancel out. Thus :



In some reactions, however, this is not the case. An example of this will now be considered.

Dissociation of Phosphorus Pentachloride.



In this reaction there is a volume change, for by Avogadro's Hypothesis each volume of pentachloride vapour on decomposing will give two volumes of mixture. Hence if a represents the initial number of molecules of pentachloride and x the number changed, giving x of trichloride and x of chlorine, when equilibrium is reached, and if V is the volume of the equilibrium mixture then :

$$\frac{\frac{x}{V} \times \frac{x}{V}}{\frac{a-x}{V}} = K \quad \text{or} \quad \frac{x^2}{(a-x)V} = K \quad . \quad . \quad . \quad (i)$$

Thus the degree of dissociation $\left(\frac{x}{a} \times 100\right)$ if expressed as a percentage depends not only on K , which varies with temperature, but also on V .

The degree of dissociation can be calculated from the vapour density of the mixture (see abnormal vapour densities, page 27).

The Effect of Increasing the Amount of One of the Products of a Reaction.

If excess of chlorine—say, y mols.—is added to the equilibrium mixture above without increasing the volume, and if x is thereby changed to x_1 , then

$$\frac{\frac{x_1}{V} \times \frac{x_1 + y}{V}}{\frac{a - x_1}{V}} = K \quad \text{or} \quad \frac{x_1(x_1 + y)}{(a - x_1)V} = K$$

Since K and V are the same as in the above equation (i), then x_1 must be less than x . The dissociation is therefore diminished in the presence of one of the constituents under these conditions, and this argument and corresponding experimental results for the vapour density were used by Wurtz as evidence for the existence of dissociation.

Similar considerations will apply to the addition of a common ion to an electrolyte ionised in solution (see page 195).

If, however, the chlorine is added to the equilibrium mixture at its own partial pressure, then its active mass and hence the degree of dissociation will remain unchanged.

Equilibrium Constant and Partial Pressures.

The molecular concentrations of gaseous substances in a mixture are clearly proportional to their partial pressures. Equilibrium constants can therefore be expressed in terms of partial pressures. Such a constant is written as Kp , and will be identical with K_c (the equilibrium constant using molecular concentrations) only if there is no volume change in the reaction.

For example



At equilibrium there are $a - x + 2x = a + x$ molecules present, and if P is the total pressure, then partial pressure of N_2O_4 , written

$$p\text{N}_2\text{O}_4, \text{ is } \frac{a - x}{a + x} \cdot P.$$

$$\text{Similarly, } p\text{NO}_2 \text{ is } \frac{2x}{a + x} \cdot P.$$

Applying the Law of Mass Action we obtain :

$$\frac{\left(\frac{2x}{a+x} \cdot P\right)^2}{\frac{a-x}{a+x} \cdot P} = Kp$$

or

$$\frac{4x^2}{a^2 - x^2} \cdot P = Kp,$$

whereas

$$K_c = \frac{4x^2}{(a-x)V}$$

Active Mass—Activity Factor.

In the original statement of the Law of Mass Action, and in the applications discussed above, the active masses have been assumed to be the molecular concentrations of the reacting substances, or some power of these concentrations. Chemical systems are, however, not ideal, and the molecules interfere with their own freedom of action. Lewis (1908) introduced the device of multiplying the molecular concentration by an '*activity coefficient*' in order to give the effective active mass.

This conception has been used and developed by Debye and Hückel in the application of the Law of Mass Action to ions and in elucidating the so-called anomalous behaviour of strong electrolytes (see page 194).

In considering abnormal results for molecular weights, as determined by ebullioscopic and cryoscopic methods, even after allowance is made for association, dissociation and hydration, the behaviour may still differ from that expected for an *ideal solution* (see page 120).

Such experimental deviations, due as stated above to molecules and ions interfering with their own freedom of movement, can be used to calculate *activity coefficients*.

Molecularity and Order of Reaction.

Examples have been quoted above to illustrate that these terms are not necessarily synonymous.

Modern research has established the view that the expression Order of Reaction should only be regarded as a mathematical form which agrees with experimental measurements.

The terms unimolecular, bimolecular, etc. are used in an attempt to elucidate the mechanism of reactions and such explanations are often too simplified and in fact incorrect (see A. F. T. Dickenson, S.S.R. Vol. XXXV).

QUESTIONS ON CHAPTER VI.

1. In an experiment to determine the rate of inversion of sugar, the following results for the polarisation angle, θ° , after time t were obtained :

Time t (in minutes)	0	10	20	30	40	80	∞
Angle θ	32.4	28.8	25.5	22.4	19.6	10.3	-14.1

Show that the reaction is unimolecular.

2. On what factors does the velocity of a chemical reaction in solution depend? It was found that a solution of cane-sugar in water was hydrolysed to the extent of 25% in 1 hr. Calculate the time taken for the sugar to be 50% hydrolysed, assuming that the reaction is unimolecular. (Oxf. Schol.)

3. How does the velocity of a chemical reaction depend on the concentration of the reacting substances? Illustrate your answer by examples, and suggest how one of your examples might be studied experimentally. (Oxf. Schol.)

4. The rate of decomposition of hydrogen peroxide may be measured by titration of small but equal portions of the solution, at given intervals of time, by means of potassium permanganate :

Time (in minutes)	0	10	20
c.c. KMnO_4 required	22.8	13.8	8.25

Show that this reaction is of the first order.

Calculate (a) the fraction of the hydrogen peroxide decomposed after 15 minutes, (b) the time required for the decomposition to be half completed.

5. The velocity constant of a unimolecular reaction $AB \longrightarrow A + B$ is 1.4×10^{-4} per sec. Explain what this statement means. In what time is half the compound AB changed into A and B ? Give an example of a reaction whose rate can be measured and describe the experiments which you would make in order to determine the velocity constant. (Oxf. Schol.)

6. What is meant by saying that the reaction of ethyl acetate with excess of sodium hydroxide is a monomolecular reaction? How would you investigate the rate of reaction experimentally? (Oxf. Schol.)

7. The following results were obtained in an experiment on the saponification of ethyl acetate by means of sodium hydroxide :
 50 c.c. of $\frac{M}{20}$ ethyl acetate and 50 c.c. of $\frac{M}{20}$ sodium hydroxide were mixed together in a flask immersed in a constant-temperature bath.

At intervals of 3 minutes, 10 c.c. portions of mixture were withdrawn and transferred to small flasks containing 10 c.c. of $\frac{M}{20}$ nitric acid. The excess of nitric acid then required v c.c. of $\frac{M}{20}$ sodium hydroxide solution for neutralisation.

Time	.	.	.	12.25	12.28	12.31	12.34	12.37	12.40
v	.	.	.	5.95	6.65	7.15	7.4	7.68	7.95

Show that the reaction is of the second order and calculate the average value of the velocity constant.

8. Explain and illustrate what is meant by the following terms as applied to a chemical reaction : (a) active mass of a reactant, (b) velocity constant, (c) equilibrium constant. (Oxf. Schol.)

9. When 1 mol. of ethyl alcohol reacts with 1 mol. of acetic acid until an equilibrium is obtained, there is then present in the solution 0.333 mol. each of alcohol and acid, and 0.666 mol. each of ester and water. Determine the amount of ester present at equilibrium when (a) 3 mols. of alcohol react with 1 mol. of acid, (b) 1 mol. of alcohol reacts with 1 mol. of acid in the presence of 1 mol. of water. (Camb. H.C.)

10. What do you understand by the term equilibrium constant? Deduce a formula for this constant in terms of the concentrations of the reacting substances.

Calculate the percentage of nitric oxide present in air heated to 2200° Abs. given that the equilibrium constant of the reaction $N_2 + O_2 \rightleftharpoons 2NO$, at this temperature, is 8.8×10^{-4} , the nitric oxide term being the numerator, and quantities being expressed in gram-molecules. (Camb. Schol.)

11. In a series of six experiments with hydrogen iodide 0.96 gm. of the latter in each experiment was entirely converted into vapour at the given temperatures and constant pressure, and then quickly cooled. The amount of iodine liberated in each experiment was determined by titration with 0.1N-sodium thiosulphate, and the volumes of the latter for corresponding temperatures were as follows :

250°	290°	330°	360°	400°	420°
13.25 c.c.	12.4 c.c.	12.0 c.c.	12.9 c.c.	14.6 c.c.	15.7 c.c.

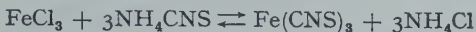
Calculate the percentage of hydrogen iodide dissociated at each temperature and express your results in the form of a graph. What conclusions do you draw from the form of the curve? (N.U.H.C.)

12. At a certain temperature 9.55 mols. of hydrogen iodide, 1.445 mols. of hydrogen, and 0.935 mol. of iodine constitute 1 litre of an equilibrium mixture. If 5 mols. of hydrogen and 3 mols. of iodine per litre are mixed at this temperature, what will be the composition of the equilibrium mixture?

13. Explain what is meant by a 'reversible reaction,' giving examples of such reactions involving (a) gases only, (b) liquids only, (c) gases and solids. Indicate the results of applying the Law of Mass Action in such cases.

After heating at 448°C . for some time, a mixture of hydrogen, iodine, and hydrogen iodide was found to contain 7.83 gm.-mols. H_2 , 1.68 gm.-mols. I_2 , and 25.54 gm.-mols. HI . If 20 gm.-mols. of hydrogen iodide gas are heated at the same temperature, what amounts of hydrogen and of iodine would be expected? Why should a change of pressure have no influence on these amounts? (Lond. H.C.)

14. State exactly what you understand by the expression :



What is the effect of adding to the system (a) ammonium thiocyanate, (b) ammonium chloride? Give your reasons. (Lond. H.C.)

15. What do you understand by the term 'equilibrium constant'? How would you investigate experimentally the equilibrium between ferric sulphate and potassium iodide in dilute sulphuric acid solution? (Oxf. Schol.)

16. Explain the terms velocity constant and equilibrium constant as applied to chemical reactions. Discuss the effect of temperature and pressure on the thermal dissociation of (a) hydrogen iodide, and (b) iodine.

In the latter case, at 1000°C . and 1 atmosphere pressure, the gas is composed of iodine atoms to the extent of 39% by volume. In order to halve this percentage, what must be the total pressure on the gas in equilibrium, the temperature remaining the same? (C.W.B., H.C.)

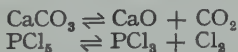
17. When 0.1 equivalent of bromine and of potassium hydroxide are dissolved in a litre of water at 0° , an equilibrium is set up as follows :



The amount of bromine present as Br_2 is 0.01 equivalent. What is the equilibrium constant for the reaction? What would be the concentration of free bromine if the mixture were made up of 1 equivalent each of bromine and potassium hydroxide per litre? Explain the principles on which your calculation depends. (Oxf. Schol.)

18. Explain, giving *three* illustrative examples, what is meant by a 'balanced reaction.' State Le Chatelier's principle and show its application in the examples you have chosen. (N.U.J.B., H.C.)

19. Discuss the reversible reactions represented by the equations :

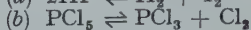


20. When steam is in contact with red-hot iron the reversible reaction may be represented by the equation :



At equilibrium at 200°C . the partial pressures of steam and hydrogen are 4.6 mm. and 95.8 mm., respectively. When the partial pressure of the steam is 6.9 mm., what is that of the hydrogen? What will be the values of these pressures if the system is under a total pressure of 760 mm.?

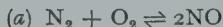
21. Describe fully and explain the effect of varying the conditions of temperature and pressure upon the following reactions :



22. What do you understand by the term 'thermal dissociation'? Describe and explain how changes in pressure affect the equilibrium between the following substances and their dissociation products: hydriodic acid, nitrogen peroxide, calcium carbonate.

Show how the degree of dissociation of nitrogen peroxide may be calculated from a knowledge of its vapour density. (Oxf. H.C.)

23. Discuss the reversible reactions :



24. Explain what you understand by *thermal dissociation*.

At 490°C . and 1 atmosphere pressure the degree of dissociation of carbonyl chloride is 0.5; calculate the vapour density under these physical conditions. Find also the change in concentration of carbonyl chloride in the gas, when 1 gm.-mol. of chlorine per original gm.-mol. of carbonyl chloride is added at constant volume. (Camb. H.C.)

CHAPTER VII

THERMOCHEMISTRY

CHEMICAL changes are nearly always accompanied by heat changes. A reaction which proceeds with evolution of heat is called an **exothermic** reaction, and one which proceeds with absorption of heat is said to be **endothermic**. The amount of heat change varies very considerably with different reactions and is expressed in calories. **1 calorie** is the heat required to raise the temperature of 1 gm. of water 1° C. (strictly from 15° C. to 16° C.). For expressing large quantities of heat the **kilogram-calorie** (often written Cal.) is often used, and is defined as the heat required to raise 1 kilogram of water 1° C.

These heat changes represent increases or decreases in the energy content of the system undergoing chemical change. Thus 1 gm. of carbon burning in oxygen to form carbon dioxide evolves approximately 8000 cals. The **intrinsic energy** of the carbon dioxide is therefore 8000 cals. less than that contained in equivalent amounts of the carbon and oxygen from which the product is obtained. Since there is no way of finding the absolute intrinsic energy, for differences only can be measured, it is customary to write the intrinsic energies of the elements as zero.

It must be remembered, however, that in the case of elements which exist in allotropic forms, the intrinsic energy will depend on which allotrope is considered. Moreover, in the case of elements and compounds, especially in the gaseous state, intrinsic energies and heats of reaction will depend on the physical conditions such as temperature and pressure.

Carbon (12 gm.) + Oxygen (32 gm.) $\longrightarrow$
 (Amorphous) Carbon dioxide, and 97,600 cals. evolved.

Carbon (12 gm.) + Oxygen (32 gm.) $\longrightarrow$
 (Graphite) Carbon dioxide, and 94,800 cals. evolved.

Similarly

Sulphur (32 gm.) $\longrightarrow$ Sulphur, and 80 cals. absorbed.
 (Rhombic) (Monoclinic)

Again Water (18 gm.) $\longrightarrow$ Steam, and 18×537 cals. absorbed.
 At 100° C. At 100° C.

Heat of Formation.

The heat of formation of a compound is the quantity of heat evolved or absorbed when 1 gm.-mol. of the compound is produced from its elements, under stated conditions.

As this cannot always be determined directly but only by calculation using the Law of Hess, it should strictly be defined as the heat which *would* be evolved or absorbed if 1 gm.-mol. *could* be produced from its elements.

Heat of Combustion.

The heat of combustion of an element or compound is the quantity of heat evolved when 1 gm.-mol. of it is completely burned in oxygen.

Heat of Reaction.

The heat of reaction is the quantity of heat evolved or absorbed when the quantities (expressed in grams) of substances represented by the chemical equation react in the direction indicated.

It should be noted that the heat changes defined as above, and as normally written, refer to quantities involved when reactions take place at *constant pressure*.

Further, the convention as to signs used in America and now adopted by the Symbols Committee of the Royal Society is:

Heat of Reaction = ΔH when heat is absorbed by the system
and = $-\Delta H$ „ „ evolved „ „

Heat of Solution.

The majority of salts on dissolving in water absorb heat. Others, especially deliquescent salts, give out heat, and this may in part be due to chemical combination. The typical salt which absorbs heat on dissolving, shows an increase of solubility with temperature, for in this way it tends to oppose the change which is applied to it from external sources. This is one of the many examples of Le Chatelier's Principle (see page 167).

The heat of solution may represent work done against molecular attractions, and partly heat of ionisation. Thus even if we start with a solution, further heat change may occur on dilution. This is referred to as **heat of dilution**. After a certain degree of dilution has taken place no more heat is absorbed on further dilution.

It should be noted that in the example quoted below (see page 165), to illustrate Hess's Law, the NH_3 solution, and the

NH_4Cl solution are assumed to have had sufficient water added for them to reach this stage. In thermochemical equations such solutions are often written $\text{NH}_3 \text{ aq.}$, $\text{NH}_4\text{Cl aq.}$)

Heat Changes at Constant Volume and at Constant Pressure.

It must be clearly understood that the observed heat change in a reaction will depend partly on whether external work is done by the system against atmospheric pressure or vice versa. When only solids and liquids are involved in the reaction, the changes in volume are small, and hence the work done on or by the system is negligible.

When gases are involved and a change of volume occurs, then we must distinguish between heat of reaction at constant volume and heat of reaction at constant pressure.

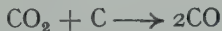
Thus if a reaction is such that there is an extra 1 gm.-mol. of gas at $T^\circ \text{ Abs.}$ produced on the right-hand side of the equation as compared with the left-hand side, then work will be done against atmospheric pressure if the reaction proceeds at constant pressure P . This work will not be done if the volume is kept constant.

The amount of work done is $PV = RT = 2T$ calories per gm.-mol. of volume V at absolute temperature T° . For an *increase* of volume equivalent to n gm.-mols. of gas the external *work done* by the system will be $2nT$ cal.

Thus the *observed heat* evolved at constant pressure, Q_P , will be *less* by this amount than that at constant volume, Q_V , since heat energy which might have been evolved is used in doing external work, *i.e.*

$$Q_P = Q_V - 2nT$$

An example of such a reaction is :



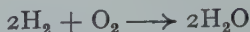
in which 1 gm.-mol.-volume of carbon dioxide gives 2 gm.-mol.-volumes of monoxide.

If, on the other hand, there is a contraction in volume when the reaction proceeds, then, at constant pressure, work will be done by the atmospheric pressure on the system.

In this case the observed heat evolved at constant pressure Q_P will be greater, by $2nT$ cal., than that at constant volume, Q_V , *i.e.* :

$$Q_P = Q_V + 2nT$$

An example of such a reaction is :



in which 3 gm.-mol.-volumes of gas on the left-hand side give 2 gm.-mol.-volumes of steam or a negligible volume of water.

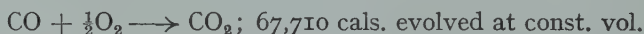
In the practical determination of heats of combustion, etc., the experiments are carried out at constant volume, and should therefore strictly be defined and stated as such.

The values given for these heat changes are, however, more frequently those at constant pressure. Moreover, the information as to whether the figures stated refer to constant volume or to constant pressure is very often not disclosed.

The student, in answering examination questions, must therefore ignore the distinction between heats at constant pressure and heats at constant volume unless directed otherwise.

Example.

The heat of combustion of carbon monoxide at constant volume is $-67,710$ cal., at 17°C . Calculate the heat of combustion at constant pressure.



In this case there is a contraction of $\frac{1}{2}$ gm.-mol.-volume per gm.-mol. of carbon monoxide burned. Hence work is done on the system by the atmospheric pressure.

$$\therefore Q_P = Q_V + 2nT$$

$$\begin{aligned} \therefore Q_P &= 67,710 + 2 \times \frac{1}{2} \times (273 + 17) \\ &= 67,710 + 290; \Delta H (\text{const. press.}) = - 68,000 \text{ cal.} \end{aligned}$$

The Law of Hess (1840).

The total heat change during a chemical change is independent of the intermediate stages, and depends only on the chemical nature and physical state of the initial substances and final products.

One experimental illustration of this law is the preparation of a dilute solution of ammonium chloride from ammonia and hydrogen chloride by two different 'routes.'

- (a) $\text{NH}_3 \text{ gas} + \text{HCl gas} = \text{NH}_4\text{Cl solid}; \Delta H = -42,000 \text{ cal.}$
 $\text{NH}_4\text{Cl solid} + \text{water} = \text{NH}_4\text{Cl solution}; \Delta H = +3,900 \text{ cal.}$

 $\text{NH}_3 \text{ gas} + \text{HCl gas} + \text{water} = \text{NH}_4\text{Cl solution}; \Delta H = -38,100 \text{ cal.}$
- (b) $\text{NH}_3 \text{ gas} + \text{water} = \text{NH}_3 \text{ solution}; \Delta H = -8,400 \text{ cal.}$
 $\text{HCl gas} + \text{water} = \text{HCl solution}; \Delta H = -17,300 \text{ cal.}$
 $\text{HCl solution} + \text{NH}_3 \text{ solution} = \text{NH}_4\text{Cl solution}; \Delta H = -12,300 \text{ cal.}$

 $\text{NH}_3 \text{ gas} + \text{HCl gas} + \text{water} = \text{NH}_4\text{Cl solution}; \Delta H = -38,000 \text{ cal.}$

These results by different 'routes' (a) and (b) are the same within the limits of experimental error.

Thus thermochemical equations may be treated as algebraic equations, and this is very important in calculating heats of reaction which cannot be measured directly.

Example.

The heat of combustion of methane is $-212,000$ cals. The heats of combustion of carbon and hydrogen are $-97,600$ cals. and $-68,400$ cals. respectively. Calculate the heat of formation of methane.

It is required to calculate ΔH in the equation :

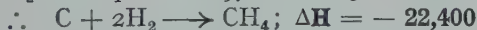
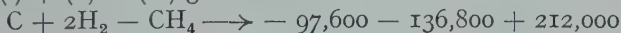


Now $\text{C} + \text{O}_2 \longrightarrow \text{CO}_2; \Delta H = -97,600 \text{ cal.}$. . . (i)

$2\text{H}_2 + \text{O}_2 \longrightarrow 2\text{H}_2\text{O}; \Delta H = -(2 \times 68,400) \text{ cal.}$ (ii)

and $\text{CH}_4 + 2\text{O}_2 \longrightarrow 2\text{H}_2\text{O} + \text{CO}_2; \Delta H = -212,000 \text{ cal.}$ (iii)

Thus (i) + (ii) - (iii) gives



Heats of Neutralisation.

The heat of neutralisation of a base by an acid is the heat in calories evolved when 1 gm.-equivalent of the base is neutralised by 1 gm.-equivalent of the acid.

Experimental Determination.

Approximate values for heats of neutralisation are easily obtained in the laboratory by the following method.

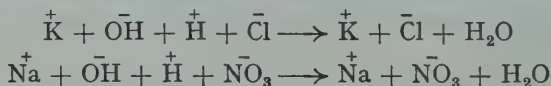
50 c.c. of normal acid and 50 c.c. of normal alkali are added together in a calorimeter fitted with stirrer and accurate thermometer. The two solutions are originally contained in separate beakers and their temperatures measured. The inner vessel of the calorimeter must be made of glass or of some metal which is not affected by the solutions.

The average temperature of the two solutions may be taken as the initial temperature, and the rise of temperature on mixing is carefully noted.

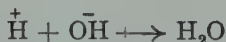
The usual corrections must be made for the water equivalent of the calorimeter and stirrer, and for heat lost by radiation, but for solutions of this strength the specific heat of the mixed solution may be taken as unity.

The results obtained for some heats of neutralisation are given in Table V, where it is seen that in many cases a value of about 13,700 cal. is obtained.

In the case of strong acids and alkalis where both the initial substances and the salts produced are completely ionised, we have :



and the heat change measured in each case is simply that of the reaction :



Hence we should expect a constant result independent of the particular acids and alkalis used provided that they are strong.

TABLE V.
Heats of Neutralisation.

Acid.	Base.	Calories.
HCl aq.	NaOH aq.	—13,700
HNO ₃ aq.	NaOH aq.	—13,680
HCl aq.	KOH aq.	—13,690
HCl aq.	NH ₄ OH aq.	—12,270
HF aq.	NaOH aq.	—16,400
HCN aq.	NH ₄ OH aq.	—1,300
HCN aq.	KOH aq.	—27,700

This constancy in experimental results is strong evidence in favour of the ionic theory.

In examples where the acid or the alkali is 'weak' a different value is obtained.

In such cases the observed heat of neutralisation will be the sum of the heat change due to the reaction $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$, and of that due to the fact that the acid and the alkali are further diluted, and hence show a *heat of ionisation*.

The latter may be either positive or negative, so that the nett heat change may be either greater or less than 13,700 cal. In Table V it will be seen that abnormal results are obtained with hydrogen fluoride, which is associated, and hydrogen cyanide, which is a very weak acid. Heat effects due to changes of hydration may also be responsible for part of the divergence from this value.

Exothermic and Endothermic Reactions.

The majority of chemical reactions are exothermic, and most compounds are exothermic compounds, that is, their heats of formation are positive. Endothermic compounds are formed from their constituent elements with absorption of energy. They are more reactive and more easily decomposed than exothermic compounds.

Typical endothermic compounds are hydrogen iodide, acetylene, nitric oxide, hydrogen peroxide, and ozone.

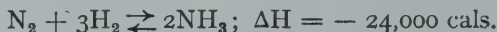
The Principle of Le Chatelier—*when a constraint is applied to a system in equilibrium the system reacts in such a way as to oppose the effects of this constraint*—may be applied to exothermic and endothermic reactions to predict the effect of changes of temperature.

In a reversible reaction a rise of temperature will accelerate the rates of the forward and the backward reaction, but not equally. The equilibrium will be moved in such a direction as to oppose the change of conditions which is applied.

Thus for an exothermic reaction a rise of temperature will be counteracted by an absorption of heat and the *yield* of product will diminish. In an endothermic reaction the converse will apply.

Examples.*Synthetic Ammonia.*

At room temperature the following equation applies :



Thus the lower the temperature the greater the yield of ammonia, but of course the rate of obtaining this yield may be too slow at low temperatures for practical purposes.

Such reactions for efficient working need a catalyst (see Chapter IX), for a catalyst will increase the rate without affecting the yield.

In this reaction there is a contraction in volume from left to right, and therefore by Le Chatelier's Principle the yield of ammonia will also be increased if the pressure is increased.

Commercially, in the Haber Process, an 'optimum' temperature of about 550° C. is used to give a good yield reasonably quickly. Pressures up to 1000 atmospheres and catalysts, such as a mixture of finely divided iron and molybdenum, are used.

Synthetic Nitric Oxide.

In this endothermic reaction both the rate and the yield will increase with rise of temperature. Pressure will not affect the equilibrium position, since there is no volume change.

Thus at 1500° C. the percentage of nitric oxide by volume in the equilibrium mixture is 0.1%, at 2000° C. it is 2%, at 3000° C. it is just over 5%.

This small yield must be cooled very rapidly to temperatures below 1500° C., at which it will only decompose slowly. At low temperatures, although the nitric oxide is unstable, its rate of decomposition is infinitely slow and therefore it may be preserved. It is said to be *metastable*. The synthesis of nitric oxide from its elements at high temperatures is used in the Birkeland-Eyde process for the fixation of atmospheric nitrogen. The cooled nitric oxide is allowed to react with the oxygen of the air below 500° C. to form nitrogen dioxide which is then absorbed in alkali.

Sulphur Trioxide.

At room temperature $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$; $\Delta H = -45,000$ cals.

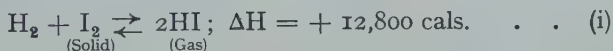
This reaction, used in the Contact Process for the manufacture of sulphuric acid, will give a good yield at low temperatures, but the rate will be slow.

An optimum temperature of about 450°C . is used together with platinised asbestos as a catalyst. High pressures would also increase the yield, but it is found that sufficiently good yields are obtained with pressures of from $1\frac{1}{2}$ to 2 atmospheres.

Thus at 430°C . the maximum yield is 99%, at 550°C . it is 85%, and at 650°C . it is 60%. These figures will vary with the pressure and these particular figures refer to conditions when air is used to oxidise the sulphur dioxide when the gases are considerably diluted with nitrogen.

Hydrogen Iodide.

At room temperature



The heat of reaction at this temperature is negative and therefore a rise of temperature will increase the yield and so diminish the degree of dissociation of hydrogen iodide.

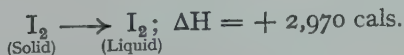
The value of the heat of formation also diminishes at higher temperatures, and above 300°C . the reaction becomes exothermic.

Thus at 375°C . equation (i) becomes :

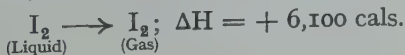


It should be noted that the second equation refers to iodine in the gaseous state. Now the latent heat of fusion of iodine is about 11.7 cal. per gm. and the latent heat of vaporisation of iodine is 24 cal. per gm. For 1 gm.-mol. these figures must be multiplied by $(2 \times 127) = 254$.

Thus at the melting point of iodine, 114°C .



and at the boiling point of iodine, 183°C .



The 'ionic product' (see page 184) for water is $[\text{H}^+] \times [\text{OH}^-]$ or $K_w = 0.61 \times 10^{-14}$ at 18°C . and $K_w = 1.06 \times 10^{-14}$ at 25°C .

Hence, in equation (ii)

$$2.3 \log_{10} \frac{0.61}{1.06} = \frac{-Q}{2} \left(\frac{1}{291} - \frac{1}{298} \right) = \frac{-Q}{2} \left(\frac{7}{291 \times 298} \right)$$

$$\therefore +Q = \frac{2.3 \times 2 \times 291 \times 298}{7} \times (\log_{10} 1.06 - \log_{10} 0.61)$$

$$= \frac{2.3 \times 2 \times 291 \times 298}{7} \times 0.24 = 13,680 \text{ cal.}$$

Thus $\text{H}^+ + \text{OH}^- \rightleftharpoons \text{H}_2\text{O}; \Delta H = -13,680$.

This agrees very closely with the experimental value obtained for the heats of neutralisation of certain acids and alkalis (see page 166), and is evidence in support of the ionic theory.

Experimental Determination of Heats of Combustion.

The substance, in tablet form, is fired electrically and burned in an atmosphere of compressed oxygen in a Berthelot bomb. Various types of bomb are in use, and a section of one is shown in Fig. 51.

This consists of a steel vessel lined with enamel and fitted with an air-tight lid.

The substance to be burned is weighed and placed in a small platinum crucible inside the bomb. A small piece of iron wire, touching the substance and connected by platinum leads to screws on the lid, can be heated electrically to start the combustion.

By means of valves, oxygen up to 25 atmospheres pressure is used in the bomb.

Before the combustion is started the bomb is placed in a calorimeter, the temperature of which is measured accurately by means of a Beckmann thermometer.

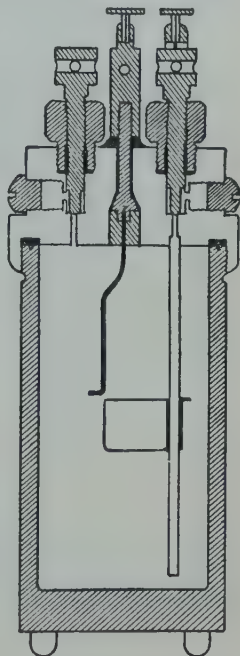


FIG. 51.—CALORIMETRIC BOMB.

The rise of temperature after combustion is observed carefully, and the usual corrections for radiation are made. The corrections necessary for the water equivalent of the calorimeter, stirrer, thermometer, and for the bomb itself, are usually determined by a separate experiment using a substance the heat of combustion of which is already known.

QUESTIONS ON CHAPTER VII.

Heats of Combustion and Formation.

1. What do you understand by the terms : (a) heat of combustion of a compound, (b) heat of formation of a compound ?

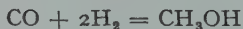
Assuming that the heats of combustion of carbon, hydrogen, and formic acid ($\text{H}\cdot\text{COOH}$) are $-97,000$ cals., $-68,000$ cals., and $-66,000$ cals., calculate the heat of formation of formic acid.

2. The heats of combustion of hydrogen, carbon, and methane are $-70,000$, $-90,000$, and $-180,000$ cals. Calculate the heat of formation of methane. (Camb. Schol.)

3. The heats of formation of sulphur dioxide and carbon dioxide are -71.0 and -94.3 Cals., respectively, and the heat of combustion of carbon disulphide is -265.1 Cals. Calculate the heat of formation of carbon disulphide. (Camb. H.C.)

4. Assuming that at 17°C . the heats of combustion of carbon monoxide and of carbon to carbon dioxide are $-67,950$ cals. and $-96,950$ cals. at constant pressure, respectively, calculate the heat of formation of carbon monoxide (a) at constant pressure, (b) at constant volume.

5. When carbon monoxide, hydrogen, and methyl alcohol are burnt completely in oxygen in closed vessels the heats evolved per gm.-mol. are $67,700$, $68,400$, and $170,600$ cals. Calculate the heat evolved in the reaction



If the reaction is carried out at atmospheric pressure at 300°C ., what work is done by the atmosphere on the system per gm.-mol. of methyl alcohol produced? What effect will this have on the heat of the reaction according as it occurs at constant volume, or at constant pressure?

(The gas constant R is 2 cals. per degree.) (Camb. Schol.)

Heats of Reaction.

6. How would you determine approximately the heat of neutralisation of an acid? The heats of neutralisation of 1 gm.-mol. of sodium hydroxide in aqueous solution by various acids are as follows : HF

—16,300 cal., HCl —13,700 cal., HBr —13,700 cal., HNO₃ —13,700 cal., CH₃COOH —13,200 cal., HCN, —2,800 cal.

Discuss and explain these results. (O. & C., H.C.)

7. Calculate the heat of the reaction :

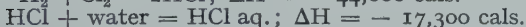
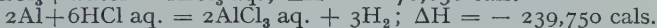
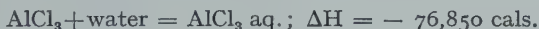


given that the heats of formation of aluminium oxide and chromium oxide are —380,000 cal. and —270,000 cal., respectively.

8. State Hess's Law and give two illustrative examples, omitting numerical data. If the heats of combustion of ethane, ethylene, and hydrogen are —370,440, —333,350, and —68,400 cal., respectively, calculate the energy change when ethylene is reduced to ethane. (Camb. 1st M.B.)

9. State the law of Hess.

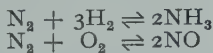
Calculate the heat of formation of anhydrous aluminium chloride from the following equations :



10. What do you mean by heats of reaction and formation? The heat of formation of phosphorus trichloride is —75,300 cal., that of water is —68,400 cal. and that of hydrochloric acid in dilute aqueous solution is —39,300 cal. The heat of reaction of phosphorus trichloride with much water is —65,000 cal. Calculate the heat of formation of phosphorous acid in dilute aqueous solution. (Camb. Schol.)

11. What do you understand by the terms (a) exothermic reaction, (b) endothermic compound?

Discuss the importance of a knowledge of heats of reaction in connection with the equations :



12. State the Principle of Le Chatelier and give examples to illustrate its application.

13. Explain, with an example in each case, the meaning of the following : (a) heat of formation, (b) exothermic compound, (c) heat of combustion, (d) heat of reaction.

The heat of formation of carbon dioxide is —94,000 cal. and that of nitrous oxide is 17,700 cal. Calculate the heat of combustion of carbon in nitrous oxide. (Lond. H.C.)

14. State the conditions under which the following pairs of substances react, and explain, in each case, what are the principal circumstances upon which the final result depends : (a) nitrogen and hydrogen, (b) hydrogen and iodine, (c) steam and carbon. (Oxf. Schol.)

CHAPTER VIII

ELECTROLYSIS AND ELECTROLYTIC DISSOCIATION

Electrolytes and Non-electrolytes.

METALS will conduct electricity to a greater or less extent, and in doing so they become heated and show other signs of physical change. Non-metals, except gas carbon, and most solid compounds are bad conductors.

In the case, however, of solutions of acids, bases, and salts in water, in alcohol, or in some other solvents, the passage of the electricity is accompanied by chemical changes. Such dissolved substances are called **electrolytes**. It is often found that these substances will conduct electricity when in the fused state.

Thus if two copper plates connected to the terminals of a battery are placed as **electrodes** in a solution of copper sulphate, copper from the positive electrode, or anode, dissolves and copper is deposited on the negative electrode or cathode. Similarly if carbon or platinum electrodes are used in a solution of hydrochloric acid, hydrogen is set free at the cathode and chlorine at the anode.

In other cases results are less straightforward. For example, the electrolysis of sodium chloride solution gives chlorine at the anode but hydrogen, and not sodium, at the cathode. This is due to the relative electrode potentials (p. 216) of the elements concerned, which also depend on the nature of the electrode.

The metals and hydrogen which are released at the cathode are said to be electropositive, and the non-metals and acid radicals which appear at the anode, or positive electrode, are electronegative.

Typical examples of electrolysis are given below, and the modern explanation in terms of electrode potentials is given on page 220.

The phenomena of electrolysis were investigated by Faraday (1832), who enunciated the following laws :

Faraday's Laws.

1. The amount of any substance liberated is proportional to the quantity of electricity which passes through the solution.

Electrolyte	Nature of Anode *	Product at Cathode (-)	Product at Anode (+)	Resulting Liquid
1. Conc. HCl soln.	C	H ₂	Cl ₂	More dilute
2. CuCl ₂ soln. .	C	Cu	Cl ₂	More dilute
3. CuCl ₂ soln. .	Copper	Cu	Cu dissolves → Cu ⁺⁺	The same
4. CuSO ₄ soln. .	Copper	Cu	Cu dissolves → Cu ⁺⁺	The same
5. CuSO ₄ soln. .	C or Pt	Cu	O ₂	H ₂ SO ₄ at anode
6. Dil. H ₂ SO ₄ soln.	C or Pt	H ₂	O ₂	More concentrated
7. <i>Molten</i> NaCl .	C	Na	Cl ₂	The same
8. Conc. NaCl soln.	C	H ₂	Cl ₂	NaOH at cathode
9. Dil. NaCl soln.	C or Pt	H ₂	O ₂	More concentrated
10. <i>Molten</i> NaOH .	C or Pt	Na	O ₂ + H ₂ O	{ More dilute, then 2Na + 2H ₂ O = 2NaOH + H ₂
11. NaOH soln. .	C or Pt	H ₂	O ₂	{ More concentrated NaOH at cathode
12. Na ₂ SO ₄ soln. .	C or Pt	H ₂	O ₂	{ H ₂ SO ₄ at anode

* The nature of the cathode is normally less important (but see p. 221).

The practical unit of electric current is *one ampere*, and 1 amp. is equal to $\frac{1}{10}$ c.g.s. unit (electromagnetic) defined in terms of the magnetic effect produced by this current. If 1 amp. passes for 1 sec., then the quantity of electricity conveyed is *one coulomb*.

Now, one coulomb is found to set free 0.001118 gm. silver, and two coulombs (*i.e.* 2 amp. for 1 sec., or 1 amp. for 2 sec.) will set free twice this amount of silver, and so on.

For practical purposes the ampere is therefore often defined as that current which will deposit 0.001118 gm. of silver, from a solution of silver nitrate, in one second.

2. The amounts of substances set free when the same quantity of electricity passes through solutions of different electrolytes are proportional to their chemical equivalents.

The mass of any element set free by the passage of one coulomb is known as its *electrochemical equivalent*.

For silver this value is, as we have seen, 0.001118. For copper it is 0.00032935, for hydrogen 0.000010446, etc.

Faraday's second law states that these quantities are proportional to the chemical equivalents, viz. silver 107.88, copper 31.78, hydrogen 1.008 (scale O = 16).

0.001118 gm. of silver is associated with the passage of 1 coulomb.
 $\therefore$ 107.88 gm. of silver are associated with the passage of

$$\frac{107.88}{0.001118} \text{ coulombs.}$$

Similarly 1.008 gm. of hydrogen is associated with the passage of

$$\frac{1.008}{0.000010446} \text{ coulombs.}$$

Each of these expressions is approximately 96,500 coulombs, and this quantity which is called one *Faraday* is associated with the gram-equivalent of any element.

Thus the atomic weight of a monovalent element will 'carry' 1 faraday and the atomic weight of a divalent element will 'carry' 2 faradays.

Theories of Electrolysis.

A satisfactory theory of electrolysis must first of all explain the fundamental facts—namely, (1) in electrolysis the chemical actions take place only at the electrodes and are observed immediately the current is applied and (2) Faraday's Laws.

Grotthus (c. 1805) suggested that the molecules of a substance in solution consisted of two parts. When electrodes are placed in the solution and a voltage is applied, then the molecules take up positions as shown in Fig. 52, and the 'positive' portion of one molecule is set free at one electrode, whilst the 'negative' portion of another is set free at the other electrode. The remaining unattached portions then take appropriate portions from neighbouring molecules. This decomposition and recombination continues throughout the solution as shown in Fig. 52.

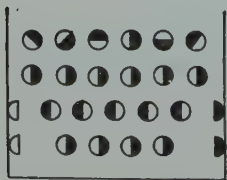


FIG. 52.

The objection to this hypothesis is that energy would be required and a voltage needed to split up these molecules whereas experiment shows that Ohm's Law applies to electrolytes. This means that all the electrical energy is used in overcoming the resistance of the solution.

Clausius (c. 1857) suggested that in all electrolytes a small proportion of the molecules was dissociated into oppositely charged atoms or radicals. The term *ion* was used by Faraday in 1834. When the current passes, these ions discharge at the electrodes, depositing atoms of the elements or taking part in secondary reactions with the solution, and further molecules dissociate to take their place.

The objection that some elements such as sodium could not exist in the presence of water is overcome by realising that the sodium atom with its positive charge is a very different thing chemically from the uncharged atom. This difference is emphasised when expressed in terms of the electronic theory (see Chapter II).

Arrhenius (c. 1887) extended the Clausius hypothesis by assuming that the fraction of the dissolved molecules ionised might be considerable, and that in dilute solutions ionisation might be complete.

He thus gave the hypothesis a quantitative basis, and from measurements of the electrical conductivity of solutions he was able to calculate to what extent a given substance in solution was ionised (see below).

It has been previously noted that certain abnormalities are obtained in the results for molecular weights of dissolved substances calculated from measurements of osmotic pressures and depressions of freezing points. These were expressed in terms of '*i*' in van 't Hoff's equation $PV = iRT$. Moreover, van 't Hoff in his theory of dilute solutions calculated degrees of dissociation from '*i*,' and obtained results which in most cases agreed closely with Arrhenius, degrees of ionisation.

Further evidence in favour of the 'Ionic Theory' will be found later in this chapter and elsewhere. Important points may be summarised now :

1. The phenomena of electrolysis—Faraday's Laws.
2. The colours of solutions—*e.g.* dilute solutions of most cupric salts are blue, owing to the presence of Cu^{++} which is blue and an anion which is usually colourless.
3. Many properties of solutions are additive—that is, the anion and the cation each make a specific contribution. This is true of electrical conductivity—also see Kohlrausch's Law of Ionic Mobilities.

4. The degrees of ionisation as calculated from van 't Hoff's 'i,' Arrhenius' conductivities, and measurements of hydrogen-ion concentration show close agreement.
5. The constancy of heats of neutralisation of acids and alkalis.
6. The phenomena of solubility product, etc., as met with in qualitative analysis.
7. The behaviour of indicators.
8. The agreement obtained between results for strengths of acids and bases (see page 202), by different methods.

The Theory of Complete Ionisation.

The weak spot in Arrhenius' theory is that it supposes relatively stable and neutral molecules to split up into oppositely charged ions as soon as the substance dissolves in water. It is sound to argue that a sodium ion will not behave chemically as does a sodium atom, but it is difficult to see how these oppositely charged ions with their mutual electrostatic attractions can be more stable than the unionised molecule. Arrhenius suggested that the ions were hydrated and possessed a great affinity for water. Other ionising solvents, such as liquid ammonia and liquid sulphur dioxide, which are known to form addition compounds, may be supposed to have affinity for ions similar to that of water.

The modern theory holds, and this is strongly supported by the evidence of X-ray analysis, that salts such as sodium chloride are completely ionised even in the solid state (see page 73). In solution, the ions previously held together by electrostatic rather than chemical bonds are easily separated, especially in a solvent such as water of high dielectric constant.

Changes which occur on dilution, and which affect osmotic pressure and conductivity measurements, are due to the fact that there is an uneven distribution of the ions in solution, and that these variations represent changes in mobility rather than in the numbers of ions present. Uneven distribution means that, owing to electrostatic attraction, there will be a group of negative ions round a positive ion and vice versa.

When a positive ion moves towards the cathode under the influence of an applied E.M.F. it gradually builds up a new 'ionic atmosphere' in front of it, whilst that behind it fades away, though more slowly. There is thus a retarding effect on the mobility of the

ion. A further retarding effect is due to the fact that the negative ionic atmosphere itself will be attracted towards the anode.

The resulting retardation of mobility will be more pronounced in more concentrated solutions, *i.e.* where the ions are closer together. Experimental results for osmotic pressure, conductivity and depression of freezing point, which depend on mobility of solute particles, will be correspondingly affected.

In dealing with the application of the Law of Mass Action to the equilibrium between ions, this uneven distribution and its effect on mobility mean that the active masses are not equal to the ionic concentrations.

By allowing for this complication and adopting the conception of an activity coefficient (see page 156) Debye and Hückel, 1923, have produced a satisfactory explanation of the so-called anomalous behaviour of 'strong' electrolytes; *i.e.* their deviations from Ostwald's Dilution Law (see page 192).

In the case of 'weak' electrolytes the number of ions relative to undissociated molecules is small and the above complication need not concern us. For weak and even for strong electrolytes it is still convenient to use Arrhenius's conception of degree of ionisation (page 189) provided that the expression **apparent** degree of ionisation is used.

We can now return to the development of the simple ionic theory by Clausius (1857), Hittorf (1855), Kohlrausch (*c.* 1876), and Arrhenius (*c.* 1887).

Migration of Ions.

In 1855 Hittorf found that during electrolysis changes of concentration occurred in the electrolyte near the electrodes. This implies that the anions move faster than the cations or vice versa. A unit positive charge is neutralised as each univalent positive ion reaches the cathode, and a corresponding unit negative charge is released at the anode. Thus, if for simplicity we assume that the elements are either deposited or set free as gases, the concentration should decrease uniformly unless the ions move with different speeds.

The connection between the relative speeds of the ions and the fall in concentration of the electrolyte is best shown by drawing a diagram (Fig. 53) on the Grotthus model.

As a simple example we may take the case of an electrolyte which gives two univalent ions, both of which on reaching the electrodes give elements which are set free and hence removed from the solution.

Further, we will assume that in this case the anion, which moves towards the anode, has a speed of $2v$, whilst that of the cation is v .

After a time the position of the ions, originally represented by (a), becomes as in (b). Two imaginary lines X and Y have been drawn enclosing a space inside which, during the time of the experiment, the concentration of the electrolyte remains unchanged. Thus in this time two negative ions have passed from right to left

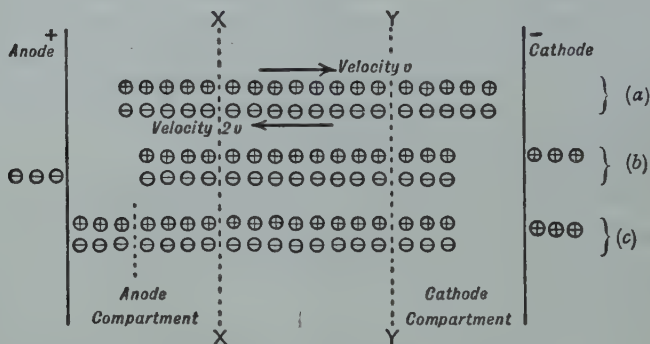


FIG. 53.—DIAGRAM TO ILLUSTRATE MIGRATION OF IONS.

across a fixed line XX , whilst one positive ion has moved in the opposite direction. Three ions of each type have been released at the electrodes.

It is clear that the amount of solute in the solution has thereby fallen from 5 mols. to 3 mols. in the cathode compartment and from 5 mols. to 4 mols. in the anode compartment.

Thus

$$\frac{\text{Speed of anion}}{\text{Speed of cation}} = \frac{2v}{v} = \frac{2}{1} =$$

and

$$\frac{\text{Speed of anion}}{\text{Sum of speeds of anion and cation}} = \frac{\text{Loss of electrolyte round cathode}}{\text{Loss of electrolyte round anode}}$$

$$\frac{\text{Speed of anion}}{\text{Sum of speeds of anion and cation}} = \frac{\text{Loss of electrolyte round cathode}}{\text{Total loss of electrolyte}}$$

The total loss of electrolyte is, of course, a measure of the current passing through the cell. The equation expressing the relationship between the changes in the amount of the electrolyte and the velocities of the ions can similarly be shown to be true for any other ratio for the velocities.

It should be noted that the loss of electrolyte at an electrode is proportional to the velocity of the ion which is *leaving* that electrode.

In the illustration above it has been assumed that both anion and cation are released at the electrodes and that the concentration of the electrolyte, at both electrodes, will therefore fall. This will not be true if chemical action occurs at the electrode.

Thus if silver nitrate solution is electrolysed between silver electrodes, then the anion (NO_3^-) on arrival at the silver anode will dissolve silver to form silver nitrate solution, which is again ionised into Ag^+ and NO_3^- .

In this case, in the anode compartment the body of the electrolyte will have moved one molecule to the right, but three 'new molecules' are formed, leaving a *nett gain* of two molecules (Fig. 53(c)). At the same time there is a *loss* of two molecules from the cathode compartment, the total amount of electrolyte remaining constant.

Transport Numbers.

The conduction of electricity through a solution is regarded as being due to the movement of the ions. Thus the quantity of electricity passing an imaginary line, such as XX , (Fig. 53) in a given time will depend on the number of anions passing in one direction and on the number of cations passing in the other direction. The quicker-moving ion will carry a larger fraction of the total current than the slower one.

Hittorf called the fraction of the current carried by anions the **transport number** of the anion = say, n . Then $1 - n$ is the fraction carried by cations and is the transport number of the cation.

If U = velocity of anion, and V = velocity of cation, then

$$n = \frac{U}{U + V} \text{ and } 1 - n = \frac{V}{U + V}$$

$$\therefore \frac{n}{1 - n} = \frac{U}{V} = \frac{\text{Loss of electrolyte round cathode}}{\text{Loss of electrolyte round anode}}$$

As explained above, in calculating these losses of electrolyte from observed values, allowances must be made for chemical reactions at the electrodes (see the case of silver nitrate above).

Experimental Measurement of Transport Numbers.

The transport numbers for Ag^+ and NO_3^- may be measured by means of the apparatus shown in Fig. 54.

The apparatus contains silver nitrate solution (approximately $N/20$) the strength of which has been accurately determined by titration with standard ammonium thiocyanate solution or by some other method.

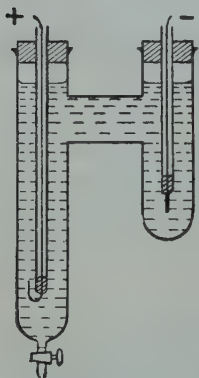


FIG. 54.—APPARATUS FOR MEASURING TRANSPORT NUMBERS.

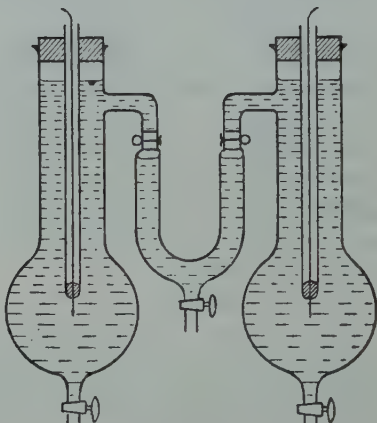


FIG. 55.—APPARATUS FOR MEASURING TRANSPORT NUMBERS.

The anode consists of a small rod of silver cemented into the hollow glass tube which carries the ordinary copper lead.

The current is allowed to pass for two or three hours and the solution round the anode is then run off and titrated. It is important to run off all that part of the solution (approximately two-thirds of the total) whose composition may have changed. The remainder should not have changed, and should be run off separately so that this may be verified.

The total current may be measured if the cathode consists of a silver plate whose weight before and after electrolysis is deter-

mined. From this and from the gain of silver nitrate round the anode the loss round the cathode can be calculated. When substituted in the above equation (page 181) these results give the transport numbers.

The total current is often measured by inserting a separate copper or silver voltameter in the circuit. The cathode in Fig. 54 need not then be weighed, and often consists of a copper electrode in a solution of copper nitrate.

A better form of the apparatus is shown in Fig. 55, in which the anode, the middle, and the cathode compartments are more distinct and can each be analysed separately.

Calculation of Transport Numbers.

Example.

A solution of silver nitrate contained 0.010 gm. silver per c.c. After electrolysis between silver electrodes with a current of 0.08 amp. for 90 minutes the anode solution, of total volume 30 c.c., was found to contain 0.55 gm. silver. Calculate the transport numbers of Ag^+ and NO_3^- .

Original solution contained 0.010 gm. Ag per c.c. = 0.3 gm. Ag per 30 c.c. (anode compartment).

Hence gain in anode compartment = 0.55 - 0.3 = 0.25 gm. Ag.
0.08 amp. for 90 × 60 sec. represents a passage of 0.08 × 90 × 60 = 432 coulombs.

Now, 96,500 coulombs correspond to 1 gm.-equivalent or 108 gm. Ag.

$$\therefore 432 \text{ coulombs correspond to } \frac{108 \times 432}{96,500} = 0.48 \text{ gm. Ag.}$$

This current will correspond to a solution of 0.48 gm. Ag from the anode.

Hence if this had not occurred, the anode compartment would not have gained 0.25 gm. Ag., but would have lost 0.48 - 0.25 = 0.23 gm. Ag.

$$\begin{aligned} \therefore \text{Transport number of } \text{Ag}^+ &= \frac{\text{This loss of electrolyte round anode}}{\text{Total current}} \\ &= \frac{0.23}{0.48} = 0.48 \end{aligned}$$

$$\therefore \text{Transport number of } \text{NO}_3^- = 1 - 0.48 = 0.52$$

It should be noted that it does not matter in what units the numerator and denominator of the expression for the transport number are expressed (gm. Ag, gm. AgNO₃, etc.), as long as they are in the same units.

Further, it should be noted that it is the *total* loss of electrolyte round an electrode that is required as numerator in the above calculation. This can only be obtained if the solution removed from the anode or cathode compartment is the whole of that part of the solution which has undergone a change in concentration. It does not, of course, matter if some of the unchanged middle compartment is included, as this will not affect the quantity of electrolyte which has changed.

Some Transport Numbers.

($\frac{N}{10}$ solutions at 18° C.)

Cations.					Anions.				
⁺ H	.	.	.	0.83	⁻ Cl	.	.	0.17 (HCl)	
⁺ Na	.	.	.	0.38	⁻ Cl	.	.	0.62 (NaCl)	
⁺ K	.	.	.	0.49	⁻ Cl	.	.	0.51 (KCl)	
⁺ Ag	.	.	.	0.47	⁻ NO ₃	.	.	0.53	
⁺⁺ Cu	.	.	.	0.38	⁻ SO ₄	.	.	0.62	

Some typical transport numbers are given in the above table. It is now accepted that ions are usually hydrated or 'solvated.' This will affect the mobility of the ion and the influences of electrostatic forces on it. As one ion may be affected more than another, the transport number may vary with the strength of the solution and with the nature of the other ions present. Transport numbers also vary with the temperature.

Visible Movement of Ions.

Measurements of transport numbers also give, as shown previously, the *relative* speeds of ions. The actual velocity will depend on the potential difference and on the distance between the electrodes. The **absolute mobility of an ion** is defined as its velocity in centimetres per second when moving under a potential gradient of 1 volt per centimetre.

Absolute mobilities may be measured by the method used by Sir Oliver Lodge.

The tube illustrated in Fig. 56 is filled with agar-agar jelly containing phenolphthalein coloured red with a little alkali.

Above the jelly the two electrodes dip into solutions of dilute sulphuric acid and sodium sulphate respectively.

When the current is passed, from anode to cathode, the hydrogen ions pass through the jelly from the anode and decolorise the phenolphthalein. The value for the absolute mobility of the hydrogen ion was thus found to be about 0.0025 cm. per sec. per unit potential gradient, and is found to be very little less in a solid jelly than in an ordinary liquid solution. For solvents other than water different values are obtained for these mobilities.



FIG. 56.—APPARATUS FOR DIRECT MEASUREMENT OF IONIC VELOCITIES.

Similar experiments may be performed with solutions such as potassium dichromate, and the movement of the colour boundary due to the $\text{Cr}_2\text{O}_7^{2-}$ ions can be timed.

When different solutions are in contact their strengths must be arranged so as to avoid discontinuity in the potential gradient. Also if a jelly is used, the experimental tube should be immersed in a water-bath, otherwise the heat generated as the current passes may be sufficient to melt the jelly.

Some recent values for absolute ionic mobilities at 18° C. in water are given below :

H^+		0.00325	OH^-		0.00178
K^+		0.00068	Cl^-		0.00068
Na^+		0.00045	NO_3^-		0.00064
Ag^+		0.00057			

An independent method for obtaining values for absolute mobilities of ions by calculation from measurements of conductivity is explained on page 191.

Conductivity of Electrolytes.

Kohlrausch (*c*, 1876), measured the conductivities of solutions of metallic salts and found that in any given case the conductivity due to a fixed amount of the salt increased as the solution was diluted. It was this discovery which led to Arrhenius' theory

(c. 1887) that salts in solution are ionised to an extent depending on the strength of the solution.

It will be remembered that Ohm's Law, which is true for electrolytic conduction, states that the current, C , which passes between two points is proportional to the potential difference, E , between them.

This constant ratio $\frac{E}{C}$ is called the resistance, R , of the substance between the points. It is proportional to the length l and inversely proportional to the area of cross section, a , of the conductor.

Thus $R = \frac{\rho \times l}{a}$, where ρ is a constant for a given material and is known as the specific resistance. ρ is obviously the value of the resistance for unit length of material of unit cross section.

The specific conductivity, s , is then equal to $\frac{1}{\rho}$, usually expressed in 'reciprocal ohms per cm.'

Measurement of the Conductivity of an Electrolyte.

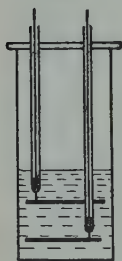


FIG. 57.—CONDUCTIVITY CELL (SOLUTIONS OF LOW CONDUCTIVITY).

The method employed is that of the Wheatstone bridge as for solid conductors. When electrolytes are used, gases may be set free at the electrodes, and they will then set up a back electromotive force. Hence an alternating current from an induction coil is used, and the electrodes are coated with platinum black. Owing to the use of an alternating current, the galvanometer normally used for detecting the 'null position' is replaced by a telephone receiver.

The conductivity cell (see Fig. 57) contains as electrodes two discs, covered with a layer of platinum black, and welded to platinum wires which are sealed through two glass tubes. These tubes contain a little mercury, into which the ordinary copper leads are dipped.

The cell-constant, k , is first determined by measuring the resistance R of a solution of $\frac{N}{10}$ or $\frac{N}{50}$ KCl whose specific conductivity, s , has been accurately determined by previous workers. The conductivity of distilled water is sufficient to affect such a reading,

and this must have been previously determined. This must be determined using specially distilled 'conductivity water.'

For the potassium chloride solution we have :

$$s = k \times \frac{1}{R}$$

When another solution of specific conductivity, s_1 , is placed in the cell and a reading, R_1 , is obtained for its resistance, then

$$s_1 = k \times \frac{1}{R_1} \text{ (where } k = s \times R \text{)}$$

In making these measurements the conductivity cell should be placed in a thermostat.

The value of the *cell constant* depends on the area of the electrodes, their distance apart and to a small extent on the volume of liquid. The measurement of the dimensions of a cell is difficult to perform accurately, and hence the above experimental method, using a solution of known conductivity, is preferred.

In the cell shown in Fig. 57 the plates are relatively large and close together, and this means a small factor for the cell constant.

This type of cell is therefore convenient when the solution in use has a high specific resistance, that is, a low specific conductivity, for then the total resistance ($R = \frac{k}{s}$) is of reasonable size for measurement.

When the liquid in use has a low specific resistance—that is, a high specific conductivity—then the total resistance can be made of convenient size for measurement, by using the type of cell shown in Fig. 58, in which the size of the electrodes is diminished and their distance apart increased.

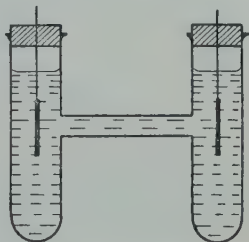


FIG. 58.—CONDUCTIVITY CELL (SOLUTIONS OF HIGH CONDUCTIVITY).

Equivalent and Molecular Conductivity.

When the conductivity of a solute is determined with solutions of varying strength, results of the type shown in Fig. 59 are ob-

tained. The more dilute the solution the less the amount of solute present, but it is ionised to a greater extent.

Conductivity depends on the speed and number of the ions. For fairly dilute solutions the frictional resistance to the movement of the ions will be practically the same as for pure water, and hence the conductivity will depend only on the number of ions.

It is therefore more instructive to think of the conductivity of



FIG. 59.

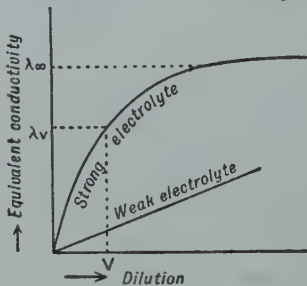


FIG. 60.

that volume of the solution which contains 1 gm.-mol. or 1 gm.-equivalent, rather than of specific conductivity.

The *molecular conductivity*, μ , is defined as the specific conductivity multiplied by the volume *in cubic centimetres*, of the solution which contains 1 gm.-mol. of solute.

The *equivalent conductivity*, λ , is the specific conductivity multiplied by the volume, *in cubic centimetres*, containing 1 gm.-equivalent.

The *dilution*, V , of a solution is the volume of solution *in litres* which contains 1 gm.-equivalent. Hence if s is the specific conductivity and λ_v is the equivalent conductivity at dilution, V , we have :

$$\lambda_v = s \times 1000 V$$

If now the equivalent (or molecular) conductivity is plotted against the dilution, curves of the type shown in Fig. 60 are obtained.

In the case of ordinary inorganic salts (so-called strong electrolytes) the equivalent conductivity reaches a maximum value, suggesting that the molecules are then completely ionised. This

follows since we have already seen that the conductivity depends on the number of ions present.

The limiting value of the equivalent conductivity is called the *equivalent conductivity at infinite dilution* and is written λ_{∞} .

If at any smaller dilution V the equivalent conductivity is λ_v , then the degree of ionisation is given by the expression :

$$\alpha = \frac{\lambda_v}{\lambda_{\infty}}$$

Solutions whose equivalent conductivities do not reach a maximum are known as weak electrolytes. The determination of λ_{∞} is not then practicable and its value for weak electrolytes is obtained by calculation (see Kohlrausch's Law, page 190).

It has already been stated that the agreement between the values of degree of ionisation obtained from depression of freezing point, etc., and from conductivity measurements is part of the evidence in favour of the ionic theory. This agreement is illustrated in the following table :

Electrolyte.	Dilution V (1 gm.-equivalent in V litres).	α from freezing points.	α from conductivity.
KCl . . .	200	0.96	0.97
	20	0.88	0.90
HNO ₃ . . .	200	0.97	0.98
	5	0.87	0.92
NaOH . . .	200	0.99	0.96
	20	0.83	0.91
Ca(NO ₃) ₂ . . .	20	0.70	0.73
	10	0.70	0.68

Example.

The equivalent conductivity of sulphuric acid at infinite dilution is 384 rec. ohms. If the specific resistance of a solution containing 15 gm. H₂SO₄ per litre is 18.4 ohms, calculate the apparent degree of ionisation of this solution.

The equivalent of H₂SO₄ = $\frac{98}{2} = 49$.

But 1000 c.c. contain 15 gm., therefore $\frac{1000 \times 49}{15}$ c.c. contain 1 equivalent.

Hence equivalent conductivity, $\lambda_v = \frac{1000 \times 49}{15} \times \frac{1}{18.4}$

$\therefore$ Apparent degree of ionisation =

$$\frac{\lambda_v}{\lambda_\infty} = \frac{1000 \times 49}{15 \times 18.4 \times 384} = 0.46.$$

Ionic Mobilities : Kohlrausch's Law.

The equivalent conductivity of an electrolyte at infinite dilution—that is, when completely ionised—must depend on the speeds of the ions, for these determine the fraction of the current carried by each type of ion and therefore the total current.

Kohlrausch confirmed experimentally that the equivalent conductivity is made up of two parts, one due to the anion and the other to the cation.

Thus

λ_∞ for NaCl	= 109	λ_∞ for KCl	= 130
λ_∞ for NaNO ₃	= 105.3	λ_∞ for KNO ₃	= 126.5
Difference	= 3.7	Difference	= 3.5

Also

λ_∞ for KCl	= 130	λ_∞ for KNO ₃	= 126.5
λ_∞ for NaCl	= 109	λ_∞ for NaNO ₃	= 105.3
Difference	= 21	Difference	= 21.2

In general, therefore, we can write

$$\lambda_\infty = \lambda_A + \lambda_K$$

and λ_A and λ_K are called the **ionic mobilities** of the anion and cation, respectively.

It is important to distinguish between ionic mobility, absolute mobility or speed (see page 184), and transport number (see page 181). They are related as follows :

$$\frac{\lambda_A}{\lambda_K} = \frac{U}{V} = \frac{n}{1 - n}$$

Also it can be shown that $U = \frac{\lambda_A}{96,500}$ and $V = \frac{\lambda_K}{96,500}$ *

Thus the ratio $\frac{\lambda_A}{\lambda_K}$ can be determined from transport number experiments; and the sum $\lambda_A + \lambda_K$ can be obtained from experimental values for λ_∞ . Therefore λ_A , λ_K , and hence U and V , can be calculated. Values for U and V may in some cases be determined independently by direct measurement (see page 184). When once one absolute mobility has been determined, all others may be obtained by measuring transport numbers or from Kohlrausch's Law.

Calculation of λ_∞ for Weak Electrolytes.

As seen above, λ_∞ for a weak electrolyte cannot be determined experimentally. It can be calculated, however, using Kohlrausch's Law.

Thus at 18° C. λ_∞ for HCl is 384 rec. ohms, λ_∞ for sodium acetate (abbreviated NaA) is 78 and λ_∞ for sodium chloride is 109 rec. ohms.

From these figures the value of λ_∞ for the weak electrolyte, acetic acid, can be calculated as follows:

By Kohlrausch's Law

$$\lambda_H + \lambda_{Cl} = 384 \quad . \quad . \quad . \quad . \quad . \quad . \quad (i)$$

$$\lambda_{Na} + \lambda_A = 78 \quad . \quad . \quad . \quad . \quad . \quad . \quad (ii)$$

$$\lambda_{Na} + \lambda_{Cl} = 109 \quad . \quad . \quad . \quad . \quad . \quad . \quad (iii)$$

$$\therefore \lambda_{HA} = \lambda_H + \lambda_A = 384 + 78 - 109 \quad . \quad . \quad (i) + (ii) - (iii) \\ = 353.$$

* Suppose that a solution of an electrolyte containing x gm.-equivalents per c.c. is contained between electrodes, of 1 sq. cm. area, 1 cm. apart, and suppose that the potential difference between these electrodes is 1 volt.

Then, if U and V are the absolute mobilities of the anion and cation, respectively, Ux anions and Vx cations will move up to the electrodes in 1 sec. There will therefore be a transfer of $(Ux + Vx) \times 96,500$ coulombs per sec., and this is the current in amps.

Moreover, the equivalent conductivity of this solution is $\lambda_\infty = \lambda_A + \lambda_K$ (if sufficiently dilute to be completely ionised). Hence the conductivity per c.c.—that is, per x equivalents—is $x(\lambda_A + \lambda_K)$. The resistance is therefore

$\frac{1}{x(\lambda_A + \lambda_K)}$ and, since the potential difference is 1 volt, the current is $x(\lambda_A + \lambda_K)$ amp.

$$\therefore (Ux + Vx) 96,500 = x(\lambda_A + \lambda_K)$$

$$\text{But} \quad \frac{U}{V} = \frac{\lambda_A}{\lambda_K}$$

$$\text{Hence} \quad U = \frac{\lambda_A}{96,500} \quad \text{and} \quad V = \frac{\lambda_K}{96,500}$$

Examples.

(1) *The transport number of the silver ion in a solution of silver nitrate is found to be 0.48. If the equivalent conductivity of silver nitrate at infinite dilution is 120 reciprocal ohms, calculate the ionic mobilities and absolute mobilities of the two ions concerned.*

$$\text{Transport number of Ag}^+ = 0.48 = \frac{V}{U+V} = \frac{\lambda_{\text{H}}}{\lambda_{\text{A}} + \lambda_{\text{H}}} = \frac{\lambda_{\text{Ag}}}{\lambda_{\text{NO}_3} + \lambda_{\text{Ag}}}$$

Also

$$120 = \lambda_{\infty} = \lambda_{\text{NO}_3} + \lambda_{\text{Ag}}$$

$\therefore$

$$\frac{\lambda_{\text{Ag}}}{120} = 0.48 \quad \therefore \lambda_{\text{Ag}} = 57.6$$

and

$$\lambda_{\text{NO}_3} = 120 - 57.6 = 62.4$$

$$\therefore \text{Absolute mobility of Ag}^+ = \frac{57.6}{96,500} = 0.0006 \text{ cm. per sec.}$$

$$\text{and Absolute mobility of NO}_3^- = \frac{62.4}{96,500} = 0.00065 \text{ cm. per sec.}$$

(2) λ_{∞} for the sodium salt of a weak organic acid, HX, is 117. If the ionic mobility of H^+ is 318 and the ionic mobility of Na^+ is 43, calculate λ_{∞} for the acid.

$$\lambda_{\infty} \text{ NaX} = 117 = \lambda_{\text{Na}} + \lambda_{\text{X}} \quad \therefore \lambda_{\text{X}} = 117 - 43 = 74$$

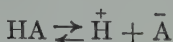
$$\text{But } \lambda_{\text{H}} = 318 \quad \therefore \lambda_{\infty} \text{ HX} = \lambda_{\text{H}} + \lambda_{\text{X}} = 318 + 74 = 392$$

Application of Law of Mass Action to Electrolytic Dissociation.

Ostwald's Dilution Law.

In a solution of an electrolyte the ions are in equilibrium with the undissociated molecules. The position of equilibrium will depend on the concentration of the solution and on the temperature, and can be defined by applying the Law of Mass Action (see Chapter VI).

Thus the equation representing the ionisation of an acid may be written



If α is the apparent degree of ionisation—that is, the fraction of original molecules of acid which are dissociated—and if V is the

dilution—that is, the volume of solution (usually in litres) which contained 1 gm.-equivalent of acid—then :

$$1 - \alpha \rightleftharpoons \alpha + \alpha$$

and therefore

$$\frac{\frac{\alpha}{V} \times \frac{\alpha}{V}}{\frac{1 - \alpha}{V}} = K \quad \text{or} \quad \frac{\alpha^2}{(1 - \alpha)V} = K.$$

K is the equilibrium constant which in the case of electrolytes is called the **dissociation constant**. This relationship between α and V is known as *Ostwald's Dilution Law*.

For very weak electrolytes in which α is very small compared with 1 we may write $\frac{\alpha^2}{V} = K$ or α is proportional to $\sqrt{V}$.

Calculation of Dissociation Constant.

For a tenth-normal solution of acetic acid the degree of ionisation at 25° C. as calculated from conductivity measurements (λ_{∞} being determined as on page 190) is 1.34%.

$$\alpha = \frac{\lambda_v}{\lambda_{\infty}} = 0.0134 \quad \text{or} \quad 1.34\%.$$

For a tenth-normal solution $V = 10$ litres.

Thus
$$K = \frac{(0.0134)^2}{(1 - 0.0134) \times 10} = 1.82 \times 10^{-5}$$

The constancy of K for *weak* solutions of acetic acid is shown by the following table:

THE IONISATION OF ACETIC ACID IN AQUEOUS SOLUTION AT 25° C.

V .	α (from conductivity measurements).	$K = \frac{\alpha^2}{(1 - \alpha)V}$.
0.334	0.0016	0.77×10^{-5}
0.672	0.0029	1.25×10^{-5}
1.977	0.0057	1.65×10^{-5}
5.374	0.0098	1.81×10^{-5}
10.753	0.0138	1.80×10^{-5}
63.26	0.0336	1.85×10^{-5}

Strong Electrolytes.

When a table similar to the above is produced for a strong electrolyte such as potassium chloride, the expression $\frac{\alpha^2}{(1 - \alpha)V}$ does not give a constant.

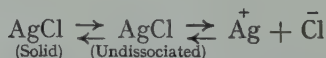
Several modifications of this equation have been suggested for strong electrolytes. Of these the empirical equation $\alpha = k\sqrt{\text{concentration}}$ i.e. $\alpha = k\sqrt{\frac{1}{V}}$, due to Kohlrausch, is the most successful. Moreover this equation holds for solvents other than water although the value of k varies with the solvent.

The theory of complete ionisation of Debye and Hückel (see page 178) when developed mathematically gives an equation which agrees with that of Kohlrausch.

It has already been noted that in applying the Law of Mass Action to such cases the 'activity' rather than the 'ionic concentration' should be used.

Solubility Product.

If we consider the case of an almost insoluble solid such as silver chloride in contact with its solution containing ions and undissociated molecules we have :



Writing $[\text{Ag}]^+$, etc., to represent the concentrations or active masses then :

$$\frac{[\text{Ag}]^+ \times [\bar{\text{Cl}}]}{[\text{AgCl}]} = K$$

This undissociated electrolyte is in contact and in equilibrium with the solid, and therefore its active mass is constant. Hence $[\text{Ag}]^+ \times [\bar{\text{Cl}}]$ is constant. This product of the ionic concentrations when excess of solid is present is known as the **solubility product**. In a solution containing different ions, when the solubility product of any pair of them (e.g. $[\text{Ag}]^+ \times [\bar{\text{Cl}}]$) is reached then, in general, precipitation will occur.

Calculation of Solubility and Solubility Product from Conductivity Measurements.

Measurements of conductivity provide a method for the determination of the solubilities of very sparingly soluble salts.

Silver chloride is very slightly soluble, and the specific conductivity of its saturated solution is found to be 1.384×10^{-6} at 25°C . Subtracting the specific conductivity, 0.054×10^{-6} , due to the water, we have 1.33×10^{-6} due to the silver chloride in solution.

Let c gm. per litre or $\frac{c}{108 + 35.5}$ gm.-equivalents per litre be the solubility of silver chloride.

Then equivalent conductivity

$$\begin{aligned} &= 1.33 \times 10^{-6} \times \text{vol. in c.c. containing 1 gm.-equivalent} \\ &= 1.33 \times 10^{-6} \times \frac{143.5 \times 1000}{c} \end{aligned}$$

Such a very weak solution may be regarded as completely ionised, and therefore its equivalent conductivity

$$= \lambda_{\infty} = \lambda_{\text{Ag}} + \lambda_{\text{Cl}} = 54 + 66 = 120$$

$$\therefore c = \frac{1.33 \times 143.5 \times 10^{-3}}{120} = 0.0016 \text{ gm. per litre}$$

$$\text{and } \frac{1.33 \times 10^{-3}}{120} = 1.1 \times 10^{-5} \text{ gm.-equivalents per litre.}$$

Assuming complete ionisation, each gm.-equivalent gives 1 gm. ion Ag and 1 gm. ion Cl.

$$\text{Hence } [\text{Ag}^+] = [\text{Cl}^-] = 1.1 \times 10^{-5}$$

$$\therefore \text{Solubility product} = [\text{Ag}^+] \times [\text{Cl}^-] = 1.2 \times 10^{-10}.$$

Phenomena Connected with Solubility Product.**The Addition of a Common Ion.**

A saturated solution of silver acetate will give a precipitate of silver acetate if the concentration of either the silver or the acetate ion is increased.

This increase in concentration may be produced by the addition of a strong solution of *silver* nitrate or of sodium *acetate*. Both

these substances are fairly highly ionised. When therefore such solutions are added to the silver acetate solution the increase in the amount of silver or acetate ion is sufficiently great relative to the increase in volume to increase the concentration of these ions.

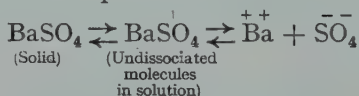
In the case of hydrogen chloride which may be added in gaseous form to a strong solution of sodium chloride the increase in concentration of chlorine ion is very rapid and salt is precipitated quickly.

Very pure sodium chloride is obtained by this method as it cannot be prepared by crystallisation from boiling water (see Chapter IV).

This principle is also applied commercially in the salting-out stage in the manufacture of soap when salt solution is added to the solution of sodium stearate. In this case precipitation is partly due to the coagulation of the soap by the addition of the electrolyte.

Washing Precipitates.

In the estimation of barium by precipitation as barium sulphate the latter must be washed free from soluble salts before it is dried. Although its solubility in water is slight, in sulphuric acid it is still less, for the presence of the sulphate ion will drive the equilibrium from right to left in the equation :



For example, the solubility product $[\text{Ba}^{++}] \times [\text{SO}_4^{--}]$ is 1×10^{-10} and the solubility is 10^{-5} gm.-mols. per litre.

If the precipitate of BaSO_4 is washed with $\frac{N}{50} \text{H}_2\text{SO}_4$ which contains 1 gm.-mol. in 100 litres, then, assuming that this weak sulphuric acid is completely ionised, the concentration of SO_4^{--} which it provides is 10^{-2} gm.-ions per litre. In comparison with this the SO_4^{--} present from barium sulphate in contact with water is negligibly small.

Since

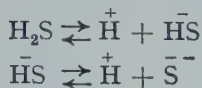
$$[\text{Ba}^{++}] \times [\text{SO}_4^{--}] = 1 \times 10^{-10} \quad \therefore [\text{Ba}^{++}] = \frac{10^{-10}}{10^{-2}} = 10^{-8}.$$

Hence washing with the sulphuric acid instead of with water reduces the loss in the proportion 10^{-5} to 10^{-8} .

Qualitative Analysis.

The variations in the solubility products of metallic sulphides determine to a considerable extent the routine of testing for metal ions in solution.

Hydrogen sulphide in solution is ionised thus :



In the presence of dilute mineral acid which provides H^+ the ionisation of H_2S will be depressed and the concentration $[\text{S}^{2-}]$ will be diminished. With ordinary bench reagents this concentration will still be sufficient to enable the solubility products to be exceeded in the cases of CuS (3×10^{-42}), HgS (3×10^{-54}) and Bi_2S_3 , As_2S_3 , Sb_2S_3 , SnS , SnS_2 , CdS , but not in those of ZnS (10^{-24}), or even NiS (10^{-27}) or MnS and CoS .

ZnS will, however, be precipitated in presence of acetic acid, since the concentration of hydrogen ions is not sufficiently great to depress the ionisation of the hydrogen sulphide so that the solubility product of the ZnS is reached. These considerations provide a basis for dividing metals into groups in qualitative analysis. Whereas those metals with very small solubility products are precipitated by hydrogen sulphide in the presence of hydrochloric acid, Zn , Mn , Co , Ni form a separate group precipitated by H_2S only in the presence of ammonium hydroxide.

Similarly ammonium hydroxide in solution is ionised thus :



The addition of ammonium chloride solution to this, by increasing the concentration $[\text{NH}_4^+]$, depresses the ionisation of the ammonium hydroxide, and hence reduces the concentration $[\text{OH}^-]$.

With ordinary bench reagents this will still be sufficient to precipitate the hydroxides $\text{Fe}(\text{OH})_3$, $\text{Cr}(\text{OH})_3$, $\text{Al}(\text{OH})_3$, but insufficient to give the larger solubility products required to precipitate the hydroxides $\text{Zn}(\text{OH})_2$, $\text{Mn}(\text{OH})_2$, etc., of the metals in subsequent groups of the analysis tables.

Another application of the idea of solubility product is provided by the fact that certain salts of weak acids, *e.g.* calcium phosphate,

are insoluble in water, but readily soluble in dilute acids. This is explained by the removal of phosphate ions by hydrogen ions from the dilute acid to form the only very slightly dissociated phosphoric acid, so that the solubility product of the calcium phosphate is not reached, *i.e.* the salt dissolves.

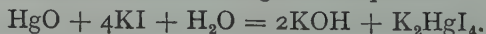
Complex Ions.

When ammonium hydroxide is added to a solution of a copper salt, a pale blue precipitate of $\text{Cu}(\text{OH})_2$ is at first obtained. On adding excess of ammonia or ammonium hydroxide, instead of still more complete precipitation of copper hydroxide occurring, the precipitate dissolves, giving a characteristic deep blue colour. This can be shown to be due to the formation of the complex cation $\text{Cu}(\text{NH}_3)_4^{++}$. Such a solution will not give a precipitate, as copper sulphate solution does, with solutions like sodium phosphate. Copper sulphide is, however, precipitated on passing hydrogen sulphide, thus proving that some Cu^{++} is present. The small number of copper ions is in equilibrium with the complex ions, but as they are removed as copper sulphide, the equilibrium is adjusted and complete precipitation ensues.

Similarly a metal may occur in a complex anion. On adding excess of potassium cyanide to a solution of silver nitrate, the original precipitate of AgCN redissolves to give $\text{K}^+ + \text{Ag}(\text{CN})_2^-$. From such a solution sodium chloride will not precipitate AgCl (solubility product 1.2×10^{-10}), but sodium sulphide will precipitate Ag_2S (solubility product 10^{-50}).

This is confirmed by the fact that the silver in a solution of silver cyanide in potassium cyanide migrates to the anion, although after secondary reactions it is eventually deposited on the cathode.

Other complex ions are $\text{Cu}(\text{CN})_3^-$, used in the separation of copper and cadmium, HgI_4^{2-} which occurs in Nessler's solution, and I_3^- present in a solution of iodine in potassium iodide. The formation of the HgI_4^{2-} ion explains the solubility of mercuric oxide, HgO , in potassium iodide according to the equation



Potassium bromide behaves similarly, but in the case of the chloride the complex ion is not of sufficient stability for the reaction to occur.

Neutrality and the Strengths of Acids and Bases.

Even the purest water shows a small conductivity. This is supposed to be due to the ionisation $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$.

The specific conductivity of water at 25°C . is approximately 0.054×10^{-6} . Hence the equivalent conductivity (18 c.c. of water = 18 gm., is the amount which, if ionised completely, gives 1 gm.-ion of H^+) is $0.054 \times 10^{-6} \times 18$.

But the equivalent conductivity at "infinite dilution"—that is, when completely ionised—is obtained from the ionic mobilities $\lambda_{\text{H}} + \lambda_{\text{OH}}$ which at 25°C . gives $349 + 196 = 545$.

$\therefore$ Degree of ionisation

$$= \frac{0.054 \times 10^{-6} \times 18}{545} = 18 \times 10^{-10} \text{ approx.}$$

Hence

1 gm.-mol. or 18 c.c. water give 18×10^{-10} gm.-ions hydrogen.

$\therefore$ 1000 c.c. water give 10^{-7} gm.-ions hydrogen.

The dissociation constant for water is therefore

$$\frac{[\text{H}^+] \times [\text{OH}^-]}{[\text{H}_2\text{O}]} = \frac{10^{-7} \times 10^{-7}}{\frac{1000}{18}}.$$

The concentration ($\frac{1000}{18}$ gm.-mols. per litre) of unionised water is so large that it may be regarded as constant, hence $[\text{H}^+] \times [\text{OH}^-]$ is a constant written $K_w = 10^{-14}$ and called the **ionic product for water**.

The value of K_w varies with the temperature, and, from this variation using van 't Hoff's equation, the heat of ionisation can be calculated (see page 171), and shown to be approximately equal to 13,700 cal.; a result in agreement with the heat of neutralisation of a strong acid and a strong base.

Strengths of Acids.

Acids were originally characterised by having a sour taste, changing the colour of various dyes, and by their action on metals. In terms of the Ionic Theory an acid in solution gives hydrogen ions.

This is also true, however, of acid salts, and if a rigid definition of the term acid is required, it is perhaps better to say that an acid is a substance which ionises to give hydrogen ions as the only positive

ions Although even this definition requires modification in terms of modern theory, it is sufficiently accurate for most purposes.

Various methods are available for comparing the strengths of acids. Methods depending on their action on metals are unreliable, since the rate of such a reaction will depend on the nature and physical condition of the metal. Thus very pure zinc will react extremely slowly with dilute sulphuric acid, whereas impure zinc is rapidly attacked by acid of the same strength. Similarly, the displacement of one acid from its salts by another depends on such properties as volatility and solubility, which vary with physical conditions, and is not therefore a fair test of strength.

Thus at ordinary temperatures sulphuric acid displaces the stronger but more volatile hydrochloric acid from its salts. At higher temperatures sulphuric acid is itself displaced by the very weak but completely non-volatile acidic oxide silica.

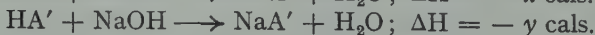
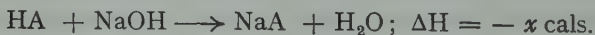
Avidities.

When two acids are allowed to compete for a base, under fair conditions, a measure of their relative avidities may be obtained.

This avidity or greediness for a base will obviously be closely related to the strength of the acid, provided that the extent to which neutralisation has occurred can be measured without the equilibrium being disturbed. Two methods for measuring avidities have been employed.

Thomsen's Thermal Method.

Heat is evolved when an acid neutralises a base, thus—



If 1 gm.-equivalent of alkali is added to a mixture of 1 gm.-equivalent of each acid, then the heat evolved will be between x and y —say, z cal.

Now, if n is the fraction of the NaOH neutralised by the HA, then $1 - n$ will be neutralised by the HA', and

$$(n \times x) + (1 - n)y = z$$

$$\therefore n = \frac{z - y}{x - y}$$

The relative strengths of the two acids are therefore

$$\frac{n}{1-n} = \frac{z-y}{x-z}.$$

In practice the heat measured is that evolved when an equivalent of one acid is added to an equivalent of a salt of the other.

Thus $\text{KCl} + \frac{1}{2}\text{H}_2\text{SO}_4 \longrightarrow \frac{1}{2}\text{K}_2\text{SO}_4 + \text{HCl}$; $\Delta H = -700$ cal.

also $\text{KOH} + \text{HCl} \longrightarrow \text{KCl} + \text{H}_2\text{O}$; $\Delta H = -13,700$ cal.

and $\text{KOH} + \frac{1}{2}\text{H}_2\text{SO}_4 \longrightarrow \frac{1}{2}\text{K}_2\text{SO}_4 + \text{H}_2\text{O}$; $\Delta H = -15,700$ cal.

By applying Hess's Law to the last two equations we see by subtraction that $\text{KCl} + \frac{1}{2}\text{H}_2\text{SO}_4 \longrightarrow \frac{1}{2}\text{K}_2\text{SO}_4 + \text{HCl}$; $\Delta H = -2,000$ cal. if the reaction is complete.

Hence the reaction is only complete from left to right to the extent $\frac{700}{2000} = 0.35$.

The relative avidities of the acids, hydrochloric and sulphuric, are therefore as $\frac{0.65}{0.35}$ or as 100 : 54.

Ostwald's Volume Method.

Just as small differences of heats of neutralisation are observed when different acids react with a base, so small differences in volume changes are observed and may be measured by means of an accurate dilatometer.

The calculation of relative avidities from such measurements is exactly similar to the above.

Strengths of Acids and Hydrogen-ion Concentration.

If the strength of an acid is due to the concentration of hydrogen ions in its solution, then it can be measured by the various methods used for estimating the latter.

Such are : (i) the apparent degree of ionisation is deduced from abnormal values for the depression of the freezing point (see page 130);

(ii) the apparent degree of ionisation is deduced from measurements of equivalent conductivity (see page 189);

(iii) the hydrogen-ion concentration is estimated from the colour changes of indicators (see page 211);

(iv) the hydrogen-ion concentration of the solution is determined from measurements of electromotive force using a hydrogen electrode (see page 217);

(v) the effect of hydrogen ions in catalysing the hydrolysis of cane-sugar or of an ester, such as methyl acetate.

The latter method is based on the assumption that the extent by which the rate of hydrolysis is accelerated is proportional to the amount of hydrogen ion present (see page 147).

The agreement obtained by various methods is shown in the following table:

Strengths of Acids.

	Avidity.	Conductivity degree of ion- isation.	Catalysis of hydrolysis of ester.
Hydrochloric Acid . .	100	100	100
Nitric Acid . .	100	99.6	91.5
Sulphuric Acid . .	49	65.0	54.5
Monochloroacetic Acid	9	4.9	4.3
Acetic Acid . .	3	0.4	0.35

In comparing the *strengths* of any two acids solutions of equivalent *concentrations* must of course be used. The above figures refer to solutions of concentration $\frac{N}{2}$.

From the discrepancies observed in results such as above and from other experimental evidence, it is now clear that the assumption that the strength of an acid is due to the presence of simple hydrogen ions is insufficient. The hydrogen ion is now regarded as being solvated, giving ions such as H_3O^+ , etc., which is called the *hydroxonium ion*, although the expression hydrogen ion is still often used for the solvated ion.

The molecule of a strong monobasic acid will therefore ionise thus:



The methods used for determining the strengths of acids are therefore more complicated in principle than was originally supposed. Thus the hydrolysis of an ester is catalysed by hydroxonium ions, molecules of undissociated acid, and also by hydroxyl

ions. The main part of the conductivity and also of the avidity of an acid is, however, due to the ions H_3O^+ .

When a non-electrolyte, such as sugar, is added to an electrolyte the results of electrolysis show that the concentrations of sugar at the electrodes become changed. This must be due to the movement of water, *i.e.* to the different amounts of water carried by the 'hydrated' anions and cations.

Strengths of Bases.

These may be determined by methods similar to those used for acids.

Methods based on electrical conductivity, depression of freezing point and avidity will depend on the degree of dissociation of the base into OH^- ions.

The saponification of an ester is normally a bimolecular reaction (see page 147), but if excess of alkali is used, its concentration remains effectively constant, and the rate of reaction will depend on the strength of the base. As in the case of acid catalysis, however, such results will also be affected by the other substances present in solution.

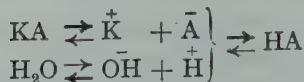
Hydrolysis of Salts.

Solutions, even of normal (as distinct from acid or basic) salts, do not necessarily give a 'neutral' solution. A 'neutral' solution contains equal concentrations of hydrogen ions and hydroxyl ions (*i.e.* $[\text{H}^+] = [\text{OH}^-]$) as in the case of pure water. The question whether it is neutral to an indicator depends on the indicator and will be discussed later (see page 211).

The salt in solution undergoes double decomposition with water to a more or less extent, producing equivalent quantities of acid and base, and the one may be stronger than the other. In terms of the Ionic Theory the acid may be more highly ionised than the base or vice versa, and this will affect the equilibrium between hydrogen ions, hydroxyl ions, and unionised water molecules.

(a) *Salts of Weak Acids and Strong Bases.*

In the case of potassium acetate which may be written as KA we have the following equations :

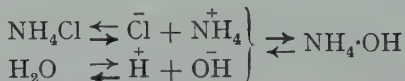


In this case the KOH is practically completely ionised and the acetic acid much less so. Hence the solution will contain $[\bar{\text{OH}}]$ greater than $[\overset{+}{\text{H}}]$ and show an alkaline reaction (to most indicators).

Similar equations may be written for salts such as sodium carbonate, potassium cyanide, and sodium sulphide, all of which give strongly alkaline solutions.

(b) *Salts of Weak Bases and Strong Acids.*

For example, the behaviour of ammonium chloride in solution may be represented as follows :



In this case the HCl is practically completely ionised, and the ammonium hydroxide much less so. The solution of ammonium chloride in water will therefore contain $[\bar{\text{H}}] > [\bar{\text{OH}}]$.

Similar equations may be written for salts of organic bases and mineral acids such as aniline hydrochloride, and for many metallic salts such as copper sulphate and ferric chloride, all of which form strongly acid solutions.

(c) *Salts of Strong Acids and Strong Bases.*

As both acid and base and the salt itself will be completely ionised in solution, the only unionised molecules present will be H_2O and hence in such solutions $[\bar{\text{H}}] = [\bar{\text{OH}}]$.

(d) *Salts of Weak Acids and Weak Bases.*

In this case unionised acid and unionised base will be present in solution, and the result will depend on their relative degrees of dissociation. The dissociation constants for ammonium hydroxide and acetic acid are approximately the same, and therefore ammonium acetate, although it is hydrolysed, gives an approximately neutral solution in which $[\bar{\text{H}}] = [\bar{\text{OH}}]$.

Since the strong base BOH is almost completely ionised, we have

$$[\bar{\text{OH}}] = \frac{x}{V}$$

Further, in any solution $[\text{H}^+] \times [\bar{\text{OH}}] = K_w$

$$\therefore K_w = K_a \times \frac{x}{(1-x)} \times \frac{x}{V} = K_a \times K_h \text{ from equation (i)}$$

For the salt of a weak base and a strong acid it can be proved similarly that

$$K_w = K_b \times K_h,$$

where K_b is the dissociation constant of the base.

If the acid and the base are both weak, then

$$K_h = \frac{K_w}{K_a \times K_b}$$

Hence K_w can be calculated if K_a and K_h or K_b and K_h are known, and conversely K_h can be calculated from a knowledge of the other two quantities. The degree of hydrolysis and hence K_h can of course be measured experimentally.

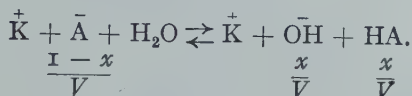
Experimental Measurement of Degree of Hydrolysis.

Since hydrolysis results in changes in the hydrogen-ion concentration of a solution, methods used for measuring the latter (see page 201) can be used for determining degrees of hydrolysis.

Any method of chemical analysis would of course disturb the equilibrium, but a method based on the principle of the Partition Coefficient is sometimes used. Thus aniline hydrochloride which hydrolyses in water into aniline and hydrogen chloride is shaken up with a mixture of water and benzene. The amount of aniline in the benzene layer is determined by precipitation with hydrogen chloride gas, the aniline hydrochloride being weighed after the benzene has been evaporated off. Since the partition coefficient of aniline between benzene and water can be separately determined, the amount of aniline (from the equivalent amount of aniline hydrochloride as weighed) found in the benzene layer will give the amount of free aniline in the water layer. This is all that is necessary for calculating the degree of hydrolysis.

Example.

Calculate (a) the hydrolysis constant, (b) the degree of hydrolysis for a deci-normal solution of potassium acetate, if the dissociation constant of acetic acid is 1.8×10^{-5} and the ionic product for water is 10^{-14} .



$$\frac{[\overset{+}{\text{H}}] \times [\bar{\text{A}}]}{[\text{HA}]} = 1.8 \times 10^{-5} \text{ and } [\overset{+}{\text{H}}] \times [\bar{\text{OH}}] = 10^{-14}.$$

Eliminating $[\overset{+}{\text{H}}]$ from the last two equations we have :

$$\frac{[\bar{\text{OH}}] \times [\text{HA}]}{[\bar{\text{A}}]} = \frac{10^{-14}}{1.8 \times 10^{-5}}$$

$$\text{Hence } K_h = \frac{x^2}{(1-x)V} = \frac{[\bar{\text{OH}}] \times [\text{HA}]}{[\bar{\text{A}}]} = \frac{10^{-14}}{1.8 \times 10^{-5}} \\ = 5.6 \times 10^{-10}$$

Further, since x is small and V is 10 litres we have

$$\frac{x^2}{10} = 5.6 \times 10^{-10}$$

$$\therefore x = \sqrt{5.6 \times 10^{-9}} = 7.5 \times 10^{-5}$$

$$\text{Hence percentage hydrolysis} = 100x = 7.5 \times 10^{-3} \\ = 0.0075\%.$$

Calculation of $[\overset{+}{\text{H}}]$ in a Solution of a Given Salt.

For a salt of a weak acid and a strong base we have the above equations (see page 205).

$$[\overset{+}{\text{H}}] = K_a \times \frac{x}{1-x} = K_a \times x \text{ if the salt is slightly hydrolysed.}$$

$$[\bar{\text{OH}}] = \frac{x}{V}$$

$$K_w = [\overset{+}{\text{H}}] \times [\bar{\text{OH}}]$$

$$\therefore [\text{H}^+] = K_a \times x = K_a \times [\text{OH}^-] \times V = K_a \times V \times \frac{K_w}{[\text{H}^+]}$$

$$\therefore [\text{H}^+] = \sqrt{K_a \times K_w \times V}$$

$$\text{and } [\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \sqrt{\frac{K_w}{K_a \times V}}$$

Similarly for a salt of a weak base and a strong acid it can be shown that

$$[\text{OH}^-] = \sqrt{K_b \times K_w \times V}$$

and

$$[\text{H}^+] = \sqrt{\frac{K_w}{K_b \times V}}$$

Examples.

1. Calculate the hydrogen-ion concentration in a decinormal solution of sodium acetate given that the dissociation constant for acetic acid is 1.8×10^{-5} .

$$K_a = 1.8 \times 10^{-5}, V = 10, K_w = 10^{-14}$$

$$\therefore [\text{H}^+] = \sqrt{K_a \times K_w \times V} = \sqrt{1.8 \times 10^{-5} \times 10^{-14} \times 10} \\ = \sqrt{1.8 \times 10^{-18}} = 1.34 \times 10^{-9} \text{ gm.-ion per litre.}$$

2. Calculate the hydrogen-ion concentration in a decinormal solution of ammonium chloride given that the dissociation constant for ammonium hydroxide is 2.3×10^{-5} .

$$K_b = 2.3 \times 10^{-5}, V = 10, K = 10^{-14}$$

$$\therefore [\text{OH}^-] = \sqrt{K_b \times K_w \times V} = \sqrt{2.3 \times 10^{-5} \times 10^{-14} \times 10} \\ = \sqrt{2.3 \times 10^{-18}} = 1.5 \times 10^{-9} \text{ gm.-ion per litre}$$

$$\therefore [\text{H}^+] = \frac{10^{-14}}{1.5 \times 10^{-9}} = 0.7 \times 10^{-5} \text{ gm.-ion per litre.}$$

Importance of Hydrogen-Ion Concentration.

It has already been noticed that hydrogen-ion concentration determines the acidity or alkalinity of a solution and that it is important in connection with certain catalytic reactions.

A knowledge of the amount of this acidity or alkalinity is also important in the chemistry of soil, in the preparation of biological cultures, in certain industrial processes such as the tanning and brewing industry, and in controlling the circulation of the blood.

Further, it is the important factor in determining the choice of indicators (see below) for use in titrations.

For these purposes there is a special conventional way of expressing the concentration of hydrogen ion in a solution—namely, as its **pH value**.

$$\text{Thus} \quad \text{pH} = \log_{10} \frac{1}{[\text{H}^+]}$$

For example, if the hydrogen-ion concentration in a solution is $[\text{H}^+] = 10^{-5}$ or 0.00001 gm.-ion per litre, then its pH value is

$$\log_{10} \frac{1}{10^{-5}} = \log_{10} 10^5 = 5.$$

For $\frac{N}{10}$ NaA solution, as above, $[\text{H}^+] = 1.34 \times 10^{-9} = 10^{-8.87}$

$$\therefore \text{pH} = \log_{10} 10^{8.87} = 8.87$$

Similarly in a $\frac{N}{10}$ NH_4Cl solution $[\text{H}^+] = 0.7 \times 10^{-5} = 10^{-5.15}$

$$\therefore \text{pH} = \log_{10} 10^{5.15} = 5.15.$$

Buffer Solutions.

As we have seen above, solutions of salts in water may have known hydrogen-ion concentrations. Still simpler examples are provided by solutions of 'strong' acids and alkalis. Thus a

solution of $\frac{N}{1000}$ HCl may be regarded as completely ionised, in

which case $[\text{H}^+] = 10^{-3}$ gm.-ion per litre and hence $\text{pH} = 3$.

Similarly, $\frac{N}{1000}$ NaOH will contain $[\text{OH}^+] = 10^{-3}$ or $\text{pH} = 11$.

When these two solutions are mixed, a strictly neutral solution of NaCl is obtained with $\text{pH} = 7$.

For use as solutions of accurately known pH value such solutions are unreliable, since their pH value changes considerably on the addition of small quantities of impurities. In pure water for which $\text{pH} = 7$, this value is also very sensitive to impurities such as carbon dioxide dissolved from the air or alkali from a glass container.

Solutions can, however, be made whose pH value is much less affected by impurities, and these are known as **buffer solutions**.

A mixture of a salt of a weak acid and the acid itself is often

used for this purpose. For example, acetic acid is weakly ionised and its sodium salt is almost completely ionised. Such a solution will therefore contain sodium ions, hydrogen ions, hydroxyl ions and acetate ions. Since sodium acetate is highly ionised the acetate ions will be in considerable excess relative to the hydrogen and hydroxyl ions. If an addition of hydrogen ions is made, these will combine with some acetate ions to form undissociated acetic acid molecules, and hence the concentration of hydrogen ions in the solution will remain practically unchanged.

Example.

A solution contains $\frac{1}{100}$ gm.-equivalent of sodium acetate and $\frac{1}{10}$ gm.-equivalent of acetic acid in a litre. Calculate its pH value if K_a for acetic acid is 1.8×10^{-5} .

$$\frac{[\overset{+}{\text{H}}] \times [\bar{\text{A}}]}{[\text{HA}]} = 1.8 \times 10^{-5}$$

and $[\text{HA}] = 10^{-1}$, since we neglect the effect on $[\text{HA}]$ of the small ionisation of acetic acid.

also $[\bar{\text{A}}] = 10^{-2}$ assuming that the sodium acetate is completely ionised.

$$\therefore [\overset{+}{\text{H}}] = \frac{1.8 \times 10^{-5} \times 10^{-1}}{10^{-2}} = 1.8 \times 10^{-4} = 10^{-3.74}$$

$$\therefore \text{pH} = 3.74$$

Conversely, we can calculate what volume of the sodium acetate to add to a given volume of the acetic acid in order to give $\text{pH} = 3$, $\text{pH} = 4$, etc.

Solutions of borax and boric acid, and of sodium dihydrogen phosphate and disodium hydrogen phosphate are also used as buffer solutions.

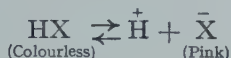
It should be realised that calculations such as the above and those in which it is required to find the volume of a solution of, say, sodium acetate of known strength to be added to a litre of, say, acetic acid of known strength in order to give a solution of given pH value, give only approximate results.

The assumptions that the sodium salt is completely ionised, and that the concentration of unionised acid is changed inappreciably, are not always justifiable. If allowance is made for these factors the calculation then becomes much more complicated and is beyond the scope of this book.

Indicators.

The simplest explanation of the behaviour of indicators was originally suggested by Ostwald. Indicators according to this explanation are either weak acids (*e.g.* phenolphthalein) or weak bases (*e.g.* methyl orange).

Phenolphthalein is regarded as a slightly ionised acid, HX.

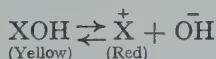


The colour change of an indicator occurs and is completed over a range from 10% ionised to 90% ionised.

Laboratory phenolphthalein is colourless—that is, less than 10% ionised.

On the addition of an alkali, the $\bar{\text{OH}}$ provided combines with some of the H^+ from the indicator, and hence the above equilibrium moves from left to right and the ionisation of the indicator is sufficient to show the pink colour of the anion. Conversely, the addition of an acid providing an increase in $[\overset{+}{\text{H}}]$ suppresses the ionisation of the indicator to give a colourless solution.

If methyl orange is regarded as a weak base we have :



This, in acid solution, will therefore give a red colour and, in alkali solution, a yellow colour.

As indicated above, the pH values corresponding to the colour changes of the various indicators may be calculated from their dissociation constants, or they may be obtained by comparison with solutions of known hydrogen-ion concentration (see page 209).

For the ordinary common indicators the working ranges are given below :

	pH.
Methyl Orange	3·0–4·5
Methyl Red	4·7–6·4
Litmus	6·5–7·5
Phenolphthalein	8·5–10·5

When the dissociation constant of an indicator is given rather than the range of its colour change in terms of pH value, it is useful to remember that a weak acid is 50% ionised when its hydrogen-ion concentration is numerically equal to its dissociation constant.

Modern Theory of Indicators.

The simple theory given above does not explain all the experimental facts. Indicators are now supposed to exist in at least two tautomeric forms, and their solutions to contain an equilibrium mixture of these forms.

For example, colourless phenolphthalein does not possess an acid structure, but on the addition of an alkali such as sodium hydroxide, the equilibrium is moved in favour of the tautomeric form which ionises as an acid and whose sodium salt gives a coloured anion.

This theory, however, does not rule out, for practical purposes, the simple treatment of the subject used above.

The Use of Indicators in Titrations.

We have previously calculated that for a $\frac{N}{10}$ solution of sodium acetate the pH value is 8.87.

Now, if 20 c.c. of $\frac{N}{5}$ acetic acid have been added to 20 c.c. $\frac{N}{5}$ sodium hydroxide, there should result 40 c.c. of $\frac{N}{10}$ sodium acetate whose pH value is 8.87.

In titrations we require to know when equivalent quantities of the acid and alkali have been added together. That is, we require to know when the solution in the titrating beaker contains the salt and water only, and not when it is strictly neutral.

In the case of the $\frac{N}{5}$ acetic acid and $\frac{N}{5}$ sodium hydroxide, we require to know when the pH value of the solution is 8.87, and not when it is 7.0. A suitable indicator which changes colour in the neighbourhood of this pH value should therefore be chosen. Phenolphthalein will therefore give a more accurate end-point than, say, litmus.

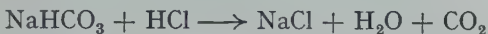
Similarly, a previous calculation showed that $\frac{N}{10}$ NH_4Cl gives $\text{pH} = 5.3$ and therefore in titrating $\frac{N}{5}$ HCl against $\frac{N}{5}$ NH_4OH the most accurate indicator will be methyl red.

Titration of Sodium Carbonate.

When a strong acid such as hydrochloric acid is added to a solution of sodium carbonate (considerably hydrolysed to give alkalinity towards indicators) a pH value of from 7 to 8 is reached when quantities have been added, represented by the equation :



With litmus, or even phenolphthalein, as indicator this end-point can be determined. On the further addition of acid the following reaction occurs :

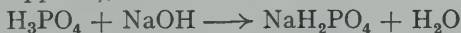


The resulting solution of carbonic acid will have a pH value from 4 to 5, and this final end-point can be determined using methyl orange or methyl red as indicator.

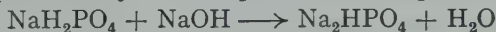
If the titration is carried out hot, the carbon dioxide is expelled, and the final solution, containing $\text{Na}^+ + \bar{\text{Cl}}$ only, will be strictly neutral, and so neutral to litmus.

Titration of Phosphoric Acid.

When a strong alkali is added to phosphoric acid, methyl orange will indicate the point when the solution contains the monosodium salt (pH = 4 approx.), thus :



On the further addition of alkali, phenolphthalein will indicate, at pH = 8 approximately, the completion of the equation :



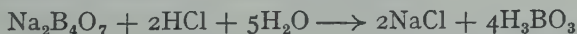
The equation



is so markedly reversible that a satisfactory titration cannot be carried out.

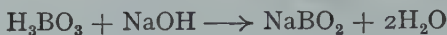
Titration of Borax.

Sodium borate (borax), like sodium carbonate, is the salt of such a weak acid that it may be titrated as a base using methyl orange as indicator, the equation being :



A solution of boric acid may, however, be titrated *as an acid* with sodium hydroxide using phenolphthalein as indicator, the presence

of mannitol or glycerine being necessary. In this titration the boric acid behaves as a monobasic acid thus :



The Changes in the pH Value of a Solution during a Titration.

If we suppose that 10 c.c. of $\frac{N}{10}$ HCl have been added to 20 c.c. of $\frac{N}{10}$ NaOH, both the acid and the alkali being strong, then we shall have 10 c.c. of unneutralised $\frac{N}{10}$ NaOH left in 30 c.c. of mixed solution.

Now, 1 litre of $\frac{N}{10}$ NaOH contains 10^{-1} gm.-ion OH^- .

$\therefore$ 10 c.c. of $\frac{N}{10}$ NaOH contain 10^{-3} gm.-ion OH^- .

$\therefore$ 1000 c.c. of resulting mixed solution contain

$$\frac{10^{-3} \times 1000}{30} \text{ gm.-ion OH.}$$

Hence in this solution $[\text{OH}^-] = 3.3 \times 10^{-2}$ and $[\text{H}^+] = \frac{10^{-14}}{[\text{OH}^-]} =$

3×10^{-13} . On the further addition of the acid, $[\text{H}^+]$ increases until when 20 c.c. have been added $[\text{H}^+] = 10^{-7}$.

From a series of such calculations a curve (see Fig. 61(a)) can be drawn showing how the pH value of the solution changes with gradually increasing amounts of acid or of alkali.

It will be noticed that the curve is 'flat' in the neighbourhood of the strictly neutral point, and that at this point small changes in the amount of alkali added give very considerable changes in the pH value. Thus this flat portion of the curve extends from pH = 4 to pH = 10 and therefore any ordinary indicator will change colour at the 'neutral' point—that is, when equivalent quantities of acid and alkali are present.

Similar curves may be drawn showing the changes in pH value when the acid is weak, or the alkali is weak or when both are weak.

The calculations of $[\text{H}^+]$ in such cases are more complicated since ionisation is incomplete and also the salt is hydrolysed. Typical results are shown in Fig. 61(b).

In the case of the weak acid and strong base the flat portion of the curve is shorter than in the case considered above. This means that the pH value of the solution in the neighbourhood of the neutral point, or point of strict equivalence, is not so susceptible to small additions of acids and alkalis (see Buffer Solutions, page 209).

Moreover, the middle of the flat portion corresponds to a pH of

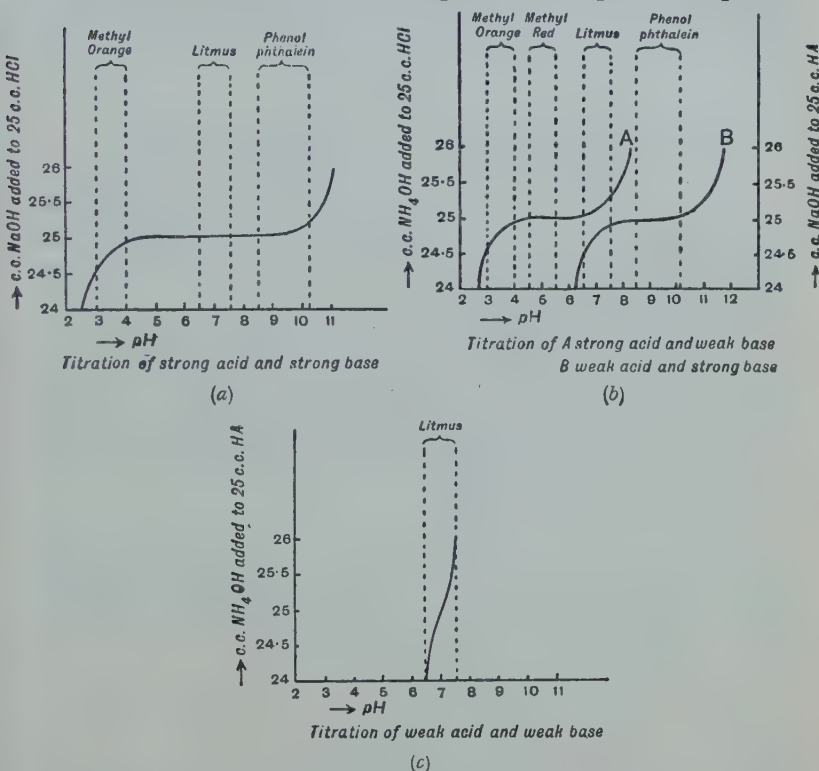


FIG. 61.—CHANGES IN pH ON ADDING BASE TO ACID (HA REPRESENTS ACETIC ACID).

8 or 9, and an indicator such as phenolphthalein will best determine this point.

A similar curve is obtained for a strong acid and a weak base, except that the position of the flat portion of the curve suggests the use of an indicator such as methyl orange.

For a weak acid and a weak base the flat portion of the curve (Fig. 61c) is so small as to be merely a point of inflexion. In this case the change in pH value with quite appreciable excess of acid or alkali is so small that no indicator will give a satisfactory end-point.

For example, if acetic acid and ammonium hydroxide are used, the point of equivalence is $\text{pH} = 7$, and if litmus is tried as indicator, the colour change may begin ($\text{pH} = 6$) when only about 24 c.c. of alkali have been added and end ($\text{pH} = 8$) when as much as 26 c.c. of alkali have been added to the 25 c.c. of acid.

Electrode Potentials and the Electrochemical Series.

When a metal is in contact with a solution of one of its salts there is a tendency for the metal to dissolve, and this is called its **solution pressure**. At the same time there is a tendency for ions of dissolved metal to be deposited on the solid metal, and this is referred to as ionic pressure.

In the case of copper and, say, copper sulphate solution, the ionic pressure is greater than the solution pressure. When therefore copper is placed in copper sulphate solution, copper ions come out of solution, deposit metallic copper, giving a positive charge to the metal and leaving an equivalent negative charge in the solution. A potential difference is thus set up and this prevents any further deposition of copper.

In the case of zinc and, say, zinc sulphate solution, the solution pressure is greater than the ionic pressure. If therefore a piece of zinc is placed in a solution of zinc sulphate, zinc dissolves, forming zinc ions, thus giving the solution a positive charge and leaving a negative charge on the solid metal.

These differences of potential between solid metals and solutions are known as **electrode potentials**.

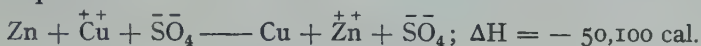
If two solutions, such as the copper sulphate and zinc sulphate above, are separated by a porous partition and the two pieces of metal are connected by a conducting wire, positive electricity will flow from copper to zinc through the wire (or negative electrons, usually represented by the symbol, ' e ' in the opposite direction). The potential differences are momentarily removed, but further solution and deposition of metal immediately occur and the process is continuous.

We thus have :



These changes occur in a Daniell Cell, and the E.M.F. of the cell is the sum of the two electrode potentials.

Chemical energy is thus converted into electrical energy, and in the case of a Daniell Cell in which no appreciable amount of heat change occurs in the working of the cell this conversion is almost 100% efficient. The E.M.F. can thus be calculated from the equation :

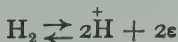


Measurement of Electrode Potentials.

** Quantitatively the electrode potential is defined as the potential difference between the metal and a solution of one of its salts into which it is dipping, the solution being of normal strength with respect to metal ions. This definition is, of course, not very practical, since, although one lead from a voltmeter can easily be connected to a copper rod dipping into copper sulphate solution, the other lead if placed in the solution will have its own electrode potential. If this lead is of copper, then clearly the voltmeter will register zero.

The measurement of the E.M.F. of a cell only gives the algebraic sum of the electrode potentials. Individual electrode potentials are therefore expressed relative to an artificial zero, *viz.* the potential of the standard hydrogen electrode. This is the potential difference obtained when hydrogen at atmospheric pressure is bubbled through a solution normal with respect to hydrogen ions (*e.g.* a normal solution of a strong acid) and in contact with a sheet of platinum foil coated with platinum black.

The platinum black acts as a catalyst in the reaction :



Measurement of Hydrogen-ion Concentration by the Hydrogen Electrode.

The value of the potential difference set up in a hydrogen electrode varies with the pressure of the hydrogen gas and with the hydrogen-ion concentration in the solution.

** Some English authors are now adopting the American practice, *viz.* the electrode potential is called *positive* when the *solution* is positively charged relative to the electrode.

If two electrodes, with two solutions of different pH, are arranged to form a cell, the E.M.F. of such a cell can be proved to be :

$$E = \frac{RT}{nF} \log_e \frac{C_1}{C_2}$$

where n is the valency of the ions, F is one faraday, C_1 and C_2 are the concentrations of the ions, and R is the gas constant.

On substituting values for F and R this equation for a temperature of 15°C. becomes :

$$E = \frac{0.058}{n} \log_{10} \frac{C_1}{C_2}$$

If one solution is normal ($C_2 = 1$) with respect to hydrogen

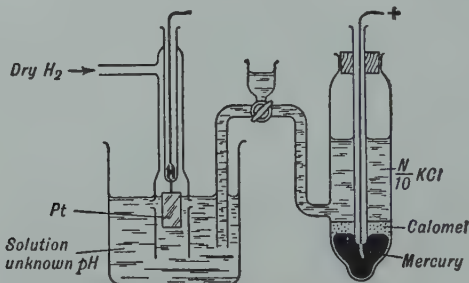


FIG. 62.—MEASUREMENT OF pH USING HYDROGEN AND CALOMEL ELECTRODES.

ion ($n = 1$), then the pH value of the other solution may be calculated from the expression $\log_{10} C_1 = \frac{E}{0.058}$.

For practical reasons a standard calomel electrode, whose potential on the hydrogen scale is accurately known, is used for measuring an unknown electrode potential (Fig. 62).

Electrometric Titrations.

A hydrogen electrode in contact with an acid solution which is being neutralised will show a sharp change in potential when the hydrogen ion is removed (as H_2O).

Similarly a piece of platinum foil in contact with a ferrous solution will give a potential which changes rapidly as the ferrous

ion is oxidised to ferric by the addition of standard potassium dichromate solution.

This method of determining an end-point eliminates the use of an external indicator.

Alternatively the hydrogen electrode may be used to standardise a buffer solution, which in turn can be used to calibrate the ordinary colour change indicators.

Some typical electrode potentials, in volts, are given below :

$\overset{+}{\text{Na}}$	.	.	.	- 2.71	$\overset{++}{\text{Cu}}$	.	.	.	+ 0.34
$\overset{+++}{\text{Al}}$	.	.	.	- 1.28	OH^-	.	.	.	+ 0.40
$\overset{++}{\text{Zn}}$	.	.	.	- 0.76	$\bar{\text{I}}$	.	.	.	+ 0.54
$\overset{++}{\text{Fe}}$	.	.	.	- 0.44	$\overset{+}{\text{Ag}}$	.	.	.	+ 0.80
$\overset{++}{\text{Sn}}$	.	.	.	- 0.14	$\bar{\text{Br}}$	.	.	.	+ 0.99
$\overset{++}{\text{Pb}}$	.	.	.	- 0.12	$\bar{\text{Cl}}$	.	.	.	+ 1.36
$\overset{+++}{\text{Fe}}$	.	.	.	- 0.04	$\overset{+}{\text{Au}}$	.	.	.	+ 1.50
$\overset{+}{\text{H}}$	.	.	.	0	$\bar{\text{F}}$	.	.	.	+ 1.90

This gives the *Electrochemical Series* which is such a useful guide to the chemical behaviour of metals.

The ease with which an element forms ions—that is, loses or gains electrons—will depend on the number of electrons in the outer shell, and it is found that electrode potentials are related to atomic numbers.

The metals, such as sodium, with a high negative electrode potential give up electrons very easily to hydrogen ions, and thus act vigorously on dilute acids and even on water :



Other elements above hydrogen in this list will also displace it from dilute acids.

Similarly iron will rust in the air. Metals such as aluminium and zinc should oxidise even more easily, but are presumably rapidly coated with a thin film of protective oxide.

Conversely, metals with positive electrode potentials do not displace hydrogen from acids, nor are they acted upon by the atmosphere.

Further, a metal such as zinc will displace a metal below it in the series from its salts, when in solution.

The metals high on the list will have a strong affinity for oxygen and sulphur, and cannot usually be obtained from their ores by reduction with carbon, nor by electrolysis of solutions of their salts. Methods based on the electrolytic decomposition of their fused salts are employed.

Galvanised iron when scratched and in contact with rain (water and carbon dioxide) forms an electrolytic cell Zinc/acid/Iron, in which the zinc will pass into solution. Under similar conditions tinfoil gives Tin/acid/Iron, but the iron passes into solution (Fe^{++} is above Sn but below Zn in the series), and rusting is very rapid when once it starts.

N.B.—In this connection it should be noted that confusion may arise because the elements with *negative* electrode potentials are often referred to as *electropositive*, since such elements tend to form positive ions (but see footnote on p. 217). In a cell supplying an E.M.F. the so-called positive current passes from the electropositive to the electronegative through the cell, and in the opposite direction through the external circuit.

In an electrolytic cell, when an E.M.F. is applied from an external source, the positive current passes from the anode (+) to the cathode (−) through the electrolyte.

During electrolysis the products set free at the electrodes set up a back E.M.F., and, for electrolysis to continue, the applied E.M.F. must reach a sufficiently high value—the **deposition or discharge potential**—to overcome this back E.M.F.

If the metal deposited on the cathode has a high solution pressure such as zinc has, then the back E.M.F. will be high, and a correspondingly high applied E.M.F. will be necessary to give a zinc deposit. With copper, whose tendency to form ions in solution is less, a much smaller applied voltage will suffice for deposition of the metal.

Metals in solution may therefore be separated if the applied E.M.F. is carefully adjusted.

According to the Electrochemical Series hydrogen should be liberated at the cathode in preference to metals such as Pb, Sn, Zn when solutions of their salts are electrolysed.

It is found, however, that most metallic electrodes (platinum is

a well known exception) have to be raised to a higher potential than indicated by the Electrochemical Series before hydrogen is set free.

The extra voltage required is called **hydrogen overvoltage**, but no satisfactory explanation of this phenomenon has yet been suggested.

The concepts of electrode and discharge potentials lead to a modification of views on the mechanism of well-known electrolytic processes. Thus in the electrolysis of sodium hydroxide sodium ions are often said to be discharged at the cathode to form sodium atoms, which in turn react with water to give hydrogen gas and sodium hydroxide. The latter, of course, ionises to give Na^+ and OH^- . The modern view is that although the sodium ions carry the current to the cathode it is the hydrogen ions, even though in very small concentration from slightly ionised water, which are discharged, since their discharge potential is lower. They are replaced by the ionisation of more water molecules.

An exception occurs when a mercury cathode is used, e.g. in the Castner-Kellner cell, since the discharge potential for sodium and mercury cathode is less than that for hydrogen. Hydrogen in fact has an overvoltage of as much as 0.8 volt at a mercury cathode.

Similarly, in the electrolysis of dilute sulphuric acid the SO_4^{--} are not now regarded as being first discharged to give SO_4 radicals, which then react with water. On the contrary, the OH^- , although in small concentration, are discharged because they require a lower discharge potential. On discharge the OH^- react to give oxygen and water :



This will occur at a platinum or carbon anode, but if the anode is copper, then the relative electrode potentials of OH^- and Cu^{++} are such that the former are not discharged, but the latter are formed by the anode going into solution.

The modern view of electrolysis is consistent with the fact that the decomposition voltages of the various acids and bases are approximately equal, *i.e.* they are determined by the discharge potentials of H^+ and OH^- , and are independent of the nature of the electrolyte.

QUESTIONS ON CHAPTER VIII.

Faraday's Laws and the Ionic Theory.

1. What is meant by the term electrochemical equivalent?
 1.584 gm. of copper are deposited in 40 minutes by a current of 2 amps. What is the electrochemical equivalent of copper?

2. In a water voltameter 55.9 c.c. of hydrogen are set free in 30 minutes. Calculate the strength of the current.

3. An electric current is passed through three cells in series containing, respectively, solutions of the following salts: copper sulphate, silver nitrate, a lead salt.

What weights of silver and lead will be deposited while 1 gm. of copper is being deposited?

Atomic weights	copper	= 63,	valency	= 2	
	silver	= 108,	"	= 1	
	lead	= 208,	"	= 2	(O.S.C.)

4. An electric current is passed between platinum plates through solutions of copper sulphate, silver nitrate, and dilute sulphuric acid, the solutions being placed in series. Explain what happens in each case.

If 0.105 gm. of copper is deposited in the first cell, calculate (a) the weight of silver separated from the second solution, (b) the volume of hydrogen, measured at 15° C. and 740 mm. which is liberated from the third solution. ($H = 1$, $Cu = 63.5$, $Ag = 108$.) (N.U.J.B., H.C.)

5. Describe and discuss the different effects that are observed when an electric current is passed through various liquids.

6. State as clearly and concisely as you can the Arrhenius' theory of electrolytic dissociation, pointing out the evidence in favour of the theory and also any facts which it fails to explain. (N.U.J.B., H.C.)

7. Discuss the objections that have been raised against the theory of electrolytic dissociation. (Camb. Schol.)

Transport Numbers.

8. A solution of silver nitrate containing 1.14 gm. of silver per litre was electrolysed between silver electrodes. The anode compartment, of volume 20 c.c., was found to contain after electrolysis 0.04 gm. of silver. A silver voltameter in series with the electrolytic cell gave a deposit of 0.032 gm. silver. What results do these figures give for the transport numbers of Ag^+ and NO_3^- ?

9. In an electrolytic cell a 0.01M solution of copper sulphate was electrolysed between copper electrodes. The anode solution of volume 25 c.c., contained after electrolysis 0.105 gm. copper sulphate, $CuSO_4$. In a copper voltameter in series with the cell 0.045 gm. of copper was deposited. Calculate the transport numbers for Cu^{++} and SO_4^{--} .

10. In the electrolysis of a solution of hydrochloric acid between cadmium electrodes the following results were obtained: Gain in chlorine round the anode and loss in chlorine round the cathode 0.00665 gm.

Silver deposited in a voltameter in series with the cell 0.1190 gm. Find the transport numbers of the hydrogen and chlorine ions ($\text{Cl} = 35.5$, $\text{Ag} = 108$). (Camb. Schol.)

11. What do you understand by transport numbers?

In an electrolysis of copper sulphate between copper electrodes, the total mass of copper deposited at the cathode was 0.153 gm. and the masses of copper per unit volume of the anode liquid before and after electrolysis were 0.79 gm. and 0.91 gm. respectively. Calculate the transport numbers for cupric and sulphate ions. (Camb. Schol.)

Conductivities.

12. Define the terms transport number, absolute mobility, equivalent conductivity, equivalent conductivity at infinite dilution, ionic mobility. Explain clearly how these quantities are related.

13. The specific resistance of a 0.01N solution of lithium chloride, LiCl , is 1064 ohm. The equivalent conductivity at infinite dilution is 101 reciprocal ohms. Calculate the apparent degree of ionisation of the given solution.

14. The specific resistance of a $\frac{1}{50}$ N potassium chloride solution at 25°C . is 361 ohms. Explain briefly what this means. What is the specific conductivity of the solution, and what is the equivalent conductivity?

What interest has the study of the equivalent conductivity of electrolytes for the chemist? (Oxf. Schol.)

15. The specific resistance of a solution of sulphuric acid, containing 14.5 gm. H_2SO_4 per litre, is 18 ohms. The equivalent conductivity at infinite dilution is 384 reciprocal ohms. What is the concentration of hydrogen ions in this solution?

16. The transport number of the nitrate ion in a solution of sodium nitrate at 18°C . is 0.59. If the equivalent conductivity of sodium nitrate solution at infinite dilution is 105.3 reciprocal ohms, calculate the ionic mobilities and the absolute mobilities of the sodium and nitrate ions.

17. State Kohlrausch's Law of Ionic Mobilities, and explain its application to the calculation of the conductivity at infinite dilution of a weak electrolyte.

18. The specific conductivity of a 0.01N solution of ammonium hydroxide at 25°C . is 1.22×10^{-4} reciprocal ohms. The ionic mobilities at 25°C . are $\text{NH}_4^+ = 70$ and $\text{OH}^- = 200$. Calculate the degree of ionisation of this solution and write down the concentration of OH^- .

19. From the following data, at 18°C. , calculate the equivalent conductivity of acetic acid at infinite dilution :

$$\lambda_{\infty} \text{ sodium acetate} = 76.4, \lambda_{\text{H}} = 314, \\ \lambda_{\infty} \text{ HCl} = 379.5, \lambda_{\infty} \text{ NaCl} = 109.$$

Ostwald's Dilution Law—Dissociation Constants.

20. The equivalent conductivities of acetic acid solutions of strengths $\frac{N}{10}$, $\frac{N}{100}$, $\frac{N}{1000}$, and at infinite dilution are 4.6, 14.3, 43.3, and 352 reciprocal ohms respectively. Show that these figures are in agreement with Ostwald's Dilution Law.

21. What is meant by the *dissociation constant* of an acid ?

Assuming the Law of Mass Action to be applicable to ionic equilibria, derive an expression connecting the degree of ionisation of an acid with the concentration of its solution.

How could the validity of such an expression be tested experimentally ? (O. & C., H.C.)

22. The molecular conductivity of acetic acid at infinite dilution is found to be 387 reciprocal ohms. At the same temperature but at a dilution of 1 gm.-mol. in 1000 litres it is 55 reciprocal ohms. What is the percentage dissociation of 0.1N acetic acid ? (Camb. Schol.)

23. Explain what is meant by the dissociation constant of a weak acid. What is the concentration of hydrogen ions in a decinormal solution of acetic acid at 18°C. , the dissociation constant at that temperature being 1.8×10^{-5} ? (O. & C., H.C.)

24. Calculate the approximate hydrogen-ion concentration in a hundredth normal solution of a monobasic acid having a dissociation constant of 10^{-6} . (Oxf. H.C.)

25. The degree of dissociation of $\frac{N}{10} \text{ NH}_4\text{OH}$ is 1.4%. Calculate the dissociation constant. What would be the concentration of hydroxyl ions in a $\frac{N}{100} \text{ NH}_4\text{OH}$ solution ?

26. The dissociation constant of a monobasic acid at a given temperature is 21.4×10^{-5} . Calculate the degree of dissociation of a decinormal solution of the acid at this temperature and the normality of the acid solution for which $\text{pH} = 2$.

27. The dissociation constant for ammonium hydroxide is 2×10^{-5} . What change in OH concentration is produced by adding 1 gm. of ammonium chloride (assumed to be completely ionised) to 200 c.c. of $\frac{N}{10} \text{ NH}_4\text{OH}$?

Solubility Product.

28. What do you understand by the term solubility product? Discuss two examples of the application of the conception of solubility product. Indicate briefly how you would determine the solubility product for lead chloride. (Oxf. Schol.)

29. The solubility of silver chloride at 18°C . is 0.0015 gm. per litre. What is its solubility product?

30. How is the term 'solubility product' defined? Give two examples of the application of this conception in ordinary qualitative analysis.

One litre of pure water dissolves 0.041 gm. of lead sulphate at 15°C . to give a saturated solution. Assuming complete dissociation of the solutes, what is the solubility of lead sulphate in $\frac{N}{100}$ sodium sulphate solution at the same temperature? An approximate result only is required. (C.W.B., H.C.)

31. State and explain the law of solubility product. What form does it take in the case of (a) silver iodide, (b) lead iodide? Give two examples to illustrate its importance in analytical chemistry.

At 25°C . a saturated solution of barium sulphate contains 2.33×10^{-4} per cent. of the salt. Calculate the solubility product and the approximate solubility of the salt in a 0.2 normal solution of ammonium sulphate. Assume all salts to be completely dissociated. (C.W.B., H.C.)

32. Explain by reference to the Ionic Theory :

(a) A concentrated solution of calcium chloride gives no precipitate with ammonium hydroxide, but with sodium hydroxide a precipitate is immediately formed.

(b) Magnesium is not precipitated from solutions of its salts by ammonium hydroxide in presence of ammonium chloride.

(c) Cupric sulphide is not precipitated by hydrogen sulphide in presence of excess of potassium cyanide, though the presence of that substance fails to prevent the precipitation of cadmium sulphide. (Oxf. Schol.)

33. From the standpoint of the ionic theory discuss the formation of a precipitate. Explain why lead sulphide is precipitated by hydrogen sulphide from acid solution while under similar conditions zinc sulphide is not precipitated. (N.U.J.B., H.C.)

34. The solubility product of silver chloride $[\text{Ag}^+][\text{Cl}^-]$ is 10^{-10} . That of silver chromate $[\text{Ag}^+]^2[\text{CrO}_4]^{--}$ is 10^{-12} .

Explain what these statements mean, and show that, when a solution of potassium chromate is to be used as an indicator in the titration of a neutral solution of a soluble chloride with silver nitrate, it should be added until its concentration is 10^{-2} molar. (Oxf. Schol.)

35. 5.85 gm. of sodium chloride were dissolved in a litre of saturated silver chloride solution. Calculate the weight of silver chloride precipitated. (The solubility of silver chloride at room temperature is 1×10^{-5} gm. molecules per litre.) (Camb. Schol.)

36. Give three examples of the utility of the concept solubility product in qualitative analysis. The solubility of barium sulphate is 2.3×10^{-4} gm. in 100 c.c. of water. What is the percentage error involved in washing a precipitate of 0.200 gm. of barium sulphate with (a) a litre of water, (b) a litre of $\frac{N}{100}$ sulphuric acid? (Camb. Schol.)

37. The dissociation constant of hydrogen sulphide for complete dissociation is 1.09×10^{-22} , the concentration of a saturated aqueous solution of the gas is 0.1, the solubility product of lead sulphide is 3.4×10^{-28} , concentrations being in gm.-mols. or gm.-atoms per litre. Find the maximum concentration of lead which can remain in $\frac{N}{10}$ HCl after it has been saturated with hydrogen sulphide. (Camb. Schol.)

Strengths of Acids and Bases.

38. Explain the meaning of the term strength as applied to acids, and describe two methods for comparing the relative strengths of acids. Show for a weak acid that the concentration of the hydrogen ions is proportional to the square root of the dissociation constant. (Camb. Schol.)

39. Justify the distinction between weak and strong acids. Explain how the strengths of acids may be compared. (Oxf. Schol.)

40. Why is hydrochloric acid said to be a stronger acid than acetic acid? Describe and explain the experiments you would perform in order to find out whether acetic acid is a stronger acid than formic acid. (Oxf. Schol.)

41. Define the term 'acid.' Explain the use of the terms 'strong' and 'weak' as applied to acids and indicate how the strength of an acid is taken into account when estimating the weight of the acid in solution. Explain why it is not possible to determine the strength of a solution of ammonia by ordinary titration with a standard solution of acetic acid. (N.U.J.B., H.C.)

42. What is meant by the strength of an acid, and what explanation is offered of the varying strengths of acids in aqueous solution? How may the strengths of acids be compared? Arrange the following acids in order of diminishing strength: hydrobromic, acetic, nitric, sulphuric, phosphoric. (Lond. H.C.)

43. 'The strength of an acid is determined by the hydrogen-ion concentration of its solution.' Comment on this statement.

44. The electrolytic dissociation constants of formic and acetic acids are 21.4×10^{-5} and 1.8×10^{-5} respectively. What are the relative avidities of the two acids?

45. Explain what is involved in the neutralisation of an acid by a base. Discuss the following facts : the heat of neutralisation of hydrochloric acid is $-13,700$ cals., but when 56 gm. of potassium hydroxide in dilute aqueous solution are treated with 34 gm. of hydrogen sulphide 7740 cals. of heat are developed. No appreciable heat is developed when a further quantity of aqueous potash is added. (O. & C., H.C.)

46. Two acids HX and HY when neutralised by a base BOH in aqueous solution give the following results for heat evolved :

	HX + BOH	31,350 cal. evolved
	HY + BOH	27,200 cal. evolved
also	BX + HY	2,740 cal. absorbed.

Calculate the relative avidities of the two acids.

47. The heats of neutralisation of nitric acid and monochloroacetic acid by sodium hydroxide are $-13,670$ and $-14,820$ cals. respectively. If one equivalent of sodium hydroxide is added to a dilute solution containing an equivalent of each of the two acids, the heat evolved is 13,950 cals.

Calculate the relative avidities of the two acids.

Hydrolysis.

48. Explain what is meant by hydrolysis. The following salts undergo hydrolysis in aqueous solution : ferric chloride, potassium cyanide, sodium carbonate, and cupric sulphate. Describe exactly how the existence of this phenomenon may be demonstrated in each case. (Camb. H.C.)

49. Calculate (a) the hydrolysis constant, (b) the degree of hydrolysis for a decinormal solution of sodium cyanide given that the dissociation constant for hydrocyanic acid is 1.3×10^{-9} .

50. What do you understand by the term hydrolysis? Exemplify your answer by reference to potassium cyanide and ammonium chloride. Describe two methods by which the degree of hydrolysis of a salt in solution may be determined. (Camb. Schol.)

51. What is the concentration of hydrogen ions in a $\frac{N}{5}$ solution of ammonium nitrate if the dissociation constant for ammonium hydroxide is 2.3×10^{-5} ?

52. Explain how the addition of one of its own salts to the solution of a weak acid will affect the hydron concentration.

Calculate the concentration of hydron in a $0.02N$ solution of a weak acid, whose ionisation constant is 10^{-6} , when its solution is $0.2N$ with respect to its sodium salt. (Oxf. Schol.)

53. State the facts which have led to the conclusion that certain substances undergo ionic dissociation in aqueous solution.

How would the hydrogen-ion concentration of a decinormal solution of hydrochloric acid change when the solution is diluted with

equal volumes of concentrated solutions of (a) sodium chloride, (b) sodium acetate? Give reasons for your statements. (Camb. 1st. M.B.)

Indicators.

54. What volume of $\frac{N}{10}$ sodium acetate solution must be added to a litre of $\frac{N}{10}$ acetic acid (dissociation constant 1.8×10^{-5}) to give a solution of $\text{pH} = 4$?

55. Discuss the behaviour of any two indicators used in volumetric analysis. What considerations determine the choice of indicator in a titration?

56. What is an 'indicator'? Give a short account of the conditions that govern the choice and behaviour of indicators in the titration of a strong acid with an alkali metal hydroxide and carbonate respectively. (N.U.J.B., H.C.)

57. What methods are available for neutralising an acid solution? Describe and explain what occurs when a solution of sodium hydroxide and sodium acetate is titrated against dilute hydrochloric acid, using as indicators (a) methyl orange, (b) litmus, (c) phenolphthalein. (Camb. Schol.)

58. What do you know of the use of (a) phenolphthalein, (b) methyl orange in acidimetry and alkalimetry? Which would you use and why, when titrating (1) lime water and HCl, (2) sodium carbonate and HCl, (3) caustic soda and oxalic acid? (Oxf. Schol.)

59. Explain the term 'hydrogen-ion concentration.' State, with reasons, the indicators you would use in titrations involving the following pairs of reagents: (a) NaHCO_3 and HCl, (b) potassium hydrogen oxalate and KOH, (c) borax and HCl, (d) AgNO_3 and KCl, (e) AgNO_3 and ammonium thiocyanate. (Oxf. Schol.)

60. The dissociation constant for butyric acid is 1.5×10^{-5} . What would be the most suitable indicator to use when titrating $\frac{N}{10}$ butyric acid against $\frac{N}{10}$ potassium hydroxide?

61. The dissociation constants for formic acid, acetic acid and benzoic acid are 2.14×10^{-4} , 1.8×10^{-5} and 6×10^{-5} respectively. What will be the effect of decinormal solutions of these acids on an indicator which changes colour at $\text{pH} = 2.5$?

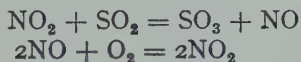
62. Why is a solution of sodium carbonate alkali? Why must phenolphthalein not be used as an indicator for titrations with sodium carbonate? (Oxf. Schol.)

CHAPTER IX

CATALYSIS

THE term catalysis is used to describe a phenomenon which is of wide occurrence in chemistry and which is met with in some quite simple reactions, with which the student is already familiar. Thus one of the first reactions met with in the study of chemistry is the preparation of oxygen by the action of heat upon potassium chlorate. It is found that the evolution of gas proceeds more rapidly and at a lower temperature if a little manganese dioxide is added to the potassium chlorate, and this effect is brought about without any permanent chemical change occurring to the manganese dioxide. Manganese dioxide is said to be a *catalyst* for this reaction.

Again, in the preparation of sulphuric acid by the oxidation of sulphur dioxide a catalyst is necessary. In the lead-chamber process nitrogen dioxide is the catalyst, and the equations for the oxidation are written in their simplest form thus :



and though these equations do not give a complete picture of the reaction, they at least suggest that the catalyst is unchanged at the end, although it takes a definite part in the process.

In the equally familiar Contact Process sulphur dioxide is oxidised directly by oxygen in the presence of platinum. At first sight it is difficult to see what part the platinum catalyst plays in the reaction, and its function is obviously different from that of the nitrogen dioxide in the chamber process.

It is apparent even from these well-known examples that catalysis is not a simple phenomenon, and that under the general term 'catalytic action' we include effects of more than one type. All catalysts, however, appear to show certain similarities, and various attempts have been made to develop criteria of catalytic action.

Characteristics of Catalytic Action.

(1). *'A catalyst is a substance which increases the rate of a reaction, but it cannot initiate a reaction nor can it alter the final equilibrium.'* Here the statement that a catalyst cannot initiate a reaction is, from the practical point of view, untrue. Thus, a mixture of hydrogen and oxygen may be perfectly stable until finely divided platinum is introduced, when combination takes place. It is usual to regard reactions such as this as taking place with infinite slowness in the absence of a catalyst, but for practical purposes this does not affect the fact that in some cases a catalyst does bring about a reaction. The proposition that the final equilibrium is unaltered must be true, for otherwise work could be obtained by the alternate introduction and removal of the catalyst, and this would violate the second law of thermodynamics.

(2). *'A catalyst is unchanged at the end of a reaction.'* This also is only partially true. Thus in the preparation of oxygen, if the manganese dioxide catalyst is added to the potassium chlorate in lumps, it will be found to be finely divided at the end of the reaction. A definite physical change has taken place in the catalyst, in this case because the manganese dioxide played a chemical part in the reaction.

(3). *'A very small amount of catalyst will bring about the reaction of indefinite amounts of the reactants.'*

This criterion of catalytic action is very often true. For instance, a very small amount of platinum will cause large amounts of sulphur dioxide and oxygen to combine. But exceptions are known—as, for example, in the Friedel-Crafts reaction, which will be discussed later—where a large quantity of the catalyst is necessary (see also page 147), although the aluminium chloride can always be recovered and used over again.

It will be seen that none of these criteria is quite rigid, though they are useful indications as to the nature of catalysis. It is impossible to obtain a perfectly rigid definition of a term employed for so complex a phenomenon, and it is better to obtain a general idea of what is included under the name 'catalysis' by considering a number of examples.

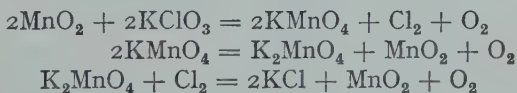
Catalytic reactions fall into two classes, which are exemplified in the two processes for the oxidation of sulphur dioxide already

referred to. In the lead-chamber process the catalyst plays a definite chemical part in the reaction, and an intermediate compound of nitrogen dioxide and sulphuric acid may be isolated. This is an example of '**chemical catalysis**,' and such catalysis usually occurs in homogeneous systems. In the contact process, however, it is difficult to imagine the platinum playing an actual chemical part in the reaction, and since a number of other very finely divided materials are active to some extent, it appears that in catalysis of this kind it is the surface of the catalyst rather than its chemical nature that is responsible for its activity. Hence this type of catalysis is spoken of as **physical** or **heterogeneous catalysis**, since it usually occurs in gas reactions on a solid catalyst. This classification of catalytic reactions, though not a rigid one, is useful in considering examples.

Examples of Chemical Catalysis.

1. The Preparation of Oxygen.

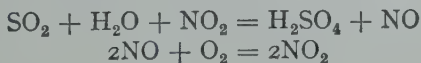
The action of manganese dioxide in catalysing the evolution of oxygen from potassium chlorate by the action of heat is more than a surface reaction, and there is evidence that an intermediate compound (probably potassium permanganate) is formed. The equations are usually written



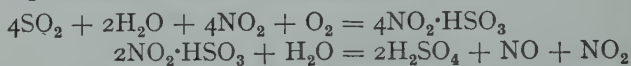
Thus besides the physical change in the aggregation of the manganese dioxide already referred to, a pink colour is often observed in the reaction mixture (suggesting the presence of permanganate), and also, the oxygen obtained by this method is frequently contaminated with chlorine.

2. The Chamber Process.

In this process to which reference has already been made, the fundamental reaction is the oxidation of sulphur dioxide to sulphuric acid with nitrogen dioxide as a catalyst, the reactions being



This is a particularly interesting example of chemical catalysis as an intermediate compound can be easily isolated. This is nitroso-sulphuric acid, or chamber crystals, and it is obtained when the supply of water in the reaction is inadequate. The equations for the chamber process are therefore more accurately written



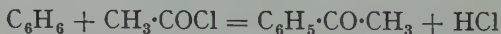
Actually the reaction is probably still more complex, and other intermediate compounds have been isolated by Raschig and others, but the main point is that there is indisputable evidence of combination between the catalyst and the reactants.

3. *The Deacon Process.*

This now obsolescent process for the preparation of chlorine involves the oxidation of hydrogen chloride by oxygen at a temperature of 350°C ., using pumice soaked in copper chloride as a catalyst. Though the mechanism of the catalysis is not altogether clear, it is probable that the cupric salt first decomposes into cuprous chloride and chlorine. A basic cupric chloride, possibly $\text{CuO}\cdot\text{CuCl}_2$, is then formed by the action of oxygen on the cuprous chloride, and cupric chloride is then regenerated by the action of hydrogen chloride upon this basic salt.

4. *The Friedel-Crafts Reaction.*

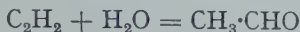
This important reaction consists in the interaction of an aromatic hydrocarbon with an organic halogen compound in the presence of anhydrous aluminium chloride as a catalyst. For example, benzene and acetyl chloride yield acetophenone by this reaction, thus:



The reaction is interesting as an example of catalysis, firstly because large amounts of aluminium chloride are required, the statement that only a very small amount of a catalyst is required breaking down in this case. Secondly, a number of compounds of aluminium chloride with reactants of the kind employed in this reaction have been isolated, and there is no doubt that the formation and decomposition of such compounds are the determining factors in the Friedel-Crafts reaction.

5. *The Addition of Water to Acetylene.*

A reaction of great commercial importance is the action of water on acetylene. Mercuric salts are used as catalysts, and it is certain that intermediate compounds are formed. The reaction is



It will be seen that acetaldehyde is produced, or in an oxidising medium, acetic acid, and both are substances of very great industrial importance.

Heterogeneous or 'Physical' Catalysis.

In the five examples that have been considered above there has been evidence that the function of the catalyst depends on the successive formation and decomposition of unstable intermediate compounds. At one time it was even supposed that all catalytic reactions depended upon such intermediate compound formation. But, as already mentioned, there are now known a very large number of catalytic reactions in which it is difficult to imagine the formation of intermediate compounds, and in which the influence of the catalyst *surface* is predominant. Before considering the possible explanation of the action of surfaces in this way, it will be best to consider some examples of this kind of catalysis, and it must be borne in mind that heterogeneous catalysis is more important because more common, especially in industry, than is chemical catalysis.

1. *The Contact Process.*

Reference has already been made to this process (see also p. 169). It consists simply in the direct oxidation of sulphur dioxide to sulphur trioxide, platinum being the catalyst. As it is the surface of the platinum which is effective, the metal must be finely divided, and platinised asbestos is therefore used. An alternative catalyst is platinised Epsom salts (Schröder-Grillo process), which is very porous and like the asbestos, presents a very large surface to the reacting gases. Iron oxide has also been used as a catalyst for this reaction (Mannheim process), but it is less effective than platinum.

2. *The Haber Process.*

This very important reaction has been already discussed (see page 168). The function of the catalyst is to cause the combination

of nitrogen and hydrogen to proceed rapidly at as low a temperature as possible, since increase of temperature, while it increases the rate of reaction, decreases the final yield of ammonia. The catalyst employed is finely divided metallic iron. It is found that the presence of molybdenum increases the catalytic activity of the iron. Molybdenum is therefore said to be a *promoter*.

3. The Oxidation of Ammonia.

Ammonia from the Haber process may be absorbed in sulphuric acid and sold as ammonium sulphate, but it is more usually oxidised to oxides of nitrogen, which are then converted into nitrates. This oxidation, like the Haber process itself, is a catalytic reaction. Air and ammonia are passed over platinum gauze, which is heated to start the reaction. Oxidation takes place with evolution of heat according to the equation



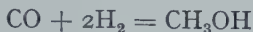
4. Hydrogenation.

Sabatier and Senderens (1897) found that unsaturated organic compounds such as ethylene ($\text{CH}_2\cdot\text{CH}_2$) could be reduced to the corresponding saturated compound (*i.e.* ethane, $\text{CH}_3\cdot\text{CH}_3$) by hydrogen in the presence of finely divided nickel as a catalyst. This reaction has been of considerable importance both in the laboratory and in industry. For example, the esters of *unsaturated* fatty acids occur widely in nature, but are of limited commercial importance, as they are liquids. They may, however, be reduced by hydrogen in the presence of minute traces of nickel to the esters of *saturated* fatty acids which are solids and of commercial importance, *e.g.* in the manufacture of margarine. Thus esters of oleic acid, $\text{C}_{17}\text{H}_{33}\cdot\text{COOH}$, pass on hydrogenation to those of stearic acid, $\text{C}_{17}\text{H}_{35}\cdot\text{COOH}$. The nickel is obtained in a fine state of subdivision by the decomposition of nickel carbonyl. Hydrogenation has other uses, and it is interesting to note that it has recently been employed quantitatively to determine the number of unsaturated ethylene bonds in complicated substances such as plant colouring matters.

5. The Synthesis of Methyl Alcohol.

The important commercial substance methyl alcohol is now synthesised by making use of a catalytic reaction. Carbon mon-

oxide and hydrogen are found to combine directly according to the equation



when they are passed, under appropriate conditions of temperature and pressure (350° C., 200 atmospheres), over certain heated metallic oxides. Zinc oxide is usually employed, and here again a promoter is employed—chromium oxide in this case.

In considering surface catalysis it must be realised that the number of surfaces which possess catalytic activity in some degree is very large indeed, though metals, particularly platinum and nickel, are much the most efficient. But it is now realised that in the majority of gas reactions the walls of the vessel play a very large part. Indeed, the number of gas reactions which are not catalysed to some extent by surfaces is small. (See Hinshelwood, *The Kinetics of Chemical Change in Gaseous Systems*.)

Since catalysis of this kind depends upon the surface of the catalyst, it would be expected that colloids would be active catalysts, since their surface area is enormous for a given mass. The activity of a colloidal metal is shown by the almost explosive violence with which colloidal platinum brings about the decomposition of hydrogen peroxide, while other finely divided substances bring it about more slowly.

The Mechanism of Surface Catalysis.

The means by which surfaces act as catalysts is not yet clear, and only a brief account of what is a very large and difficult subject can be given here. It is well known that many substances (*e.g.* charcoal) have the power of absorbing considerable volumes of gases, and it was suggested by Faraday that catalytic activity was connected with absorption or condensation of the gas on the surface of the catalyst. The process of absorption is now known to be more complex than it appears at first sight. The first process that occurs when a gas comes in contact with a solid is known as **adsorption**, and consists of the formation of a thin film, often only one molecule in thickness, on the surface of the solid. This is followed by the slower **absorption** in which greater quantities of the gas diffuse into the pores of the substance. The whole process should strictly be spoken of as 'sorption.' The work of Langmuir,

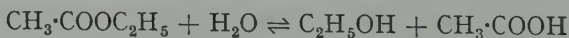
Freundlich, and others has shown that the monomolecular layer of adsorbed gas is very firmly held by the surface atoms of the substance, and that it is on the formation of this layer that catalysis probably depends, whence it is clear that the catalyst must be very finely divided so as to provide a large area for adsorption.

The actual way in which adsorption on a solid surface assists a reaction is not altogether clear, and several factors probably contribute. The mere bringing into close contact of reactant molecules must play some part, as Faraday realised. Another factor may be the taking up by the catalyst of the heat of reaction of the molecules of the product, preventing their decomposition and activating other molecules of reactant. Further, the actual arrangement of the molecules adsorbed on the catalyst surface may play a part in their reactivity. It will be seen that any hard-and-fast distinction between chemical and physical catalysis tends to break down when the mechanism of adsorption is considered.

The adsorption theory throws some light on the phenomenon known as the 'poisoning' of catalysts. In the contact process arsenical impurities have to be very carefully removed from the sulphur dioxide, as they cause very rapid loss of activity in the platinum catalyst. Substances such as arsenic or hydrogen cyanide, which deactivate catalysts, are spoken of as '*catalyst poisons*,' and it is interesting to note that they are also powerful poisons to the animal body. The mechanism of catalyst poisoning doubtless depends on the fact that these substances are powerfully and preferentially adsorbed on the surface of the catalyst and prevent the adsorption and consequent reaction of molecules of the reactants.

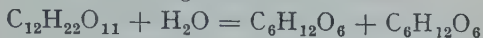
Ions as Catalysts.

One other type of catalysis remains to be mentioned—catalysis by ions. A well-known example of a catalytic reaction is the hydrolysis of an ester. The hydrolysis, for example, of ethyl acetate which proceeds according to the equation



is catalysed by both hydrogen ions and hydroxyl ions (see page 147).

The inversion of cane-sugar (see page 144) by which sucrose is converted into a mixture of glucose and fructose



is another example of catalysis by hydrogen ions. This type of catalysis is of particular interest, as the concentration of the catalyst determines the rate of the reaction, and by observing the rate of inversion the concentration of hydrogen ions in a solution may be determined. It has, however, been shown more recently that neutral salt molecules also have a catalytic effect in reactions of this type. It is certain that the action of ions as catalysts is 'chemical'—that is to say, unstable intermediate addition compounds of ions with reactant molecules are formed.

In some reactions the products are themselves catalysts for the reaction. Such reactions are said to be **autocatalytic**. Instead of showing a gradually decreasing velocity as the reaction proceeds, the reaction shows an acceleration before the final slowing down. Thus the decomposition of arsine is catalysed by arsenic, so that the curve obtained by plotting the rate of change against the time shows a maximum.

In conclusion it may be mentioned that examples are known in which the presence of certain substances not only does not hasten a reaction, but actually slows it down or inhibits it altogether. Thus a solution of a sulphite, which would normally oxidise rapidly to a sulphate, is rendered stable by the presence of traces of glycerol. Glycerol is said to be a **negative catalyst** for this reaction. A number of such examples are known, though the explanation of the phenomenon is obscure. Surfaces may behave as negative catalysts in gas reactions, and here it is doubtless because they break the chains of reacting molecules by absorbing energy which would otherwise be handed on from product to reactant.

Photochemistry.

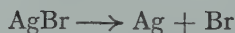
Although strictly not part of the phenomenon of catalysis, the effects produced by light on chemical changes may be conveniently considered here. Though the fact that light can initiate or modify certain chemical changes has been known for some time, the explanation of the part it plays is still only very partial and obscure, and little more than a list of reactions can be given here.

1. The Interaction of Hydrogen and Chlorine.

This is one of the best-known photochemical reactions. In the dark, hydrogen and chlorine scarcely react at all. In diffused light the reaction $\text{H}_2 + \text{Cl}_2 \longrightarrow 2\text{HCl}$ proceeds quite slowly, but in bright light the change may be explosive in character. The reaction also shows an *induction period* before reaction starts, due probably to the presence of impurities, which have to be destroyed by the chlorine. Water vapour is necessary for the reaction to proceed, but oxygen, on the other hand, tends to stop the reaction. This reaction will be referred to again.

2. The Decomposition of Silver Halides.

One of the first known photochemical changes was the darkening of silver chloride, bromide or iodide on exposure to light. This reaction is of particular importance as it is, of course, the basis of the chemistry of photography. The fundamental reaction involved seems to be the simple decomposition



3. The Synthesis of Carbohydrates.

This remarkable reaction is that by which carbon dioxide and water react in the presence of light, and is that by which sugars, starches, and celluloses are built up in the living plant. The general equation is :

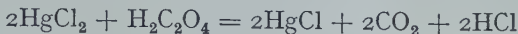


It was at one time thought that the primary photochemical reaction is the formation of formaldehyde and oxygen followed by the polymerisation of the former to carbohydrate, but there is no direct evidence to support this view.

The photochemical synthesis of formaldehyde in this way has in fact been accomplished *in the laboratory*, but the mechanism by which the whole series of changes occurs *in the living plant* is still very obscure, particularly as the green colouring matter, chlorophyll, undoubtedly plays a part.

4. The Interaction of Oxalic Acid and Mercuric Chloride.

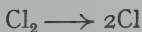
This reaction proceeds according to the equation



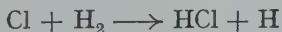
and is a photochemical reaction. Its velocity varies with the intensity of the light, and it has been used as a *chemical photometer* (Eder), since the mercurous chloride may be weighed.

In addition to these reactions for the starting of which light is required, there are others in which the nature of the products is dependent on the presence or absence of light. Thus the *chlorination of toluene* in bright sunlight produces substitution in the side-chain, forming $\text{C}_6\text{H}_5\cdot\text{CH}_2\text{Cl}$, etc., while in the absence of sunlight, substitution in the nucleus occurs, yielding *o*- and *p*-chlorotoluenes.

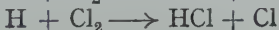
The mechanism of photochemical reactions is still far from clear, but the primary process seems to be the **activation** of reactant molecules by light energy—that is to say, energy absorbed from the incident light gives the molecules sufficient impetus to enable them to react. By the quantum theory, energy is absorbed or given out in units or *quanta*. **Einstein's Law of Photochemical Equivalence** states that each quantum of light absorbed activates one molecule of reactant. Hence the number of molecules reacting should be directly proportional to the number of quanta absorbed. In actual fact, the behaviour of photochemical reactions is by no means as simple as this, and Einstein's Law is rarely obeyed. In some reactions the *photochemical efficiency* is too low, but in others it is very high indeed; that is to say, a large number of molecules react for each quantum absorbed. It seems likely that there is in all photochemical reactions some primary change to which Einstein's Law does apply, but that secondary reactions then occur which invalidate it. Thus in the photochemical reaction between chlorine and hydrogen many thousands of molecules react for each quantum absorbed. It seems probable that the primary photochemical reaction is



The chlorine atoms then react thus :



followed by



and so on.

A *chain* of reactions is set up. Such chain reactions have in recent years been much studied, but in the hydrogen-chlorine reaction the question is complicated by the large part played by impurities.

QUESTIONS ON CHAPTER IX.

1. Write a short account of catalytic processes. Illustrate your answer by reactions of which you have personal experience in the laboratory. (Oxf. Schol.)
2. Describe four reactions of industrial importance in which the presence of a catalyst is required. What explanations have been offered of the action of catalysts? (N.U.J.B., H.C.)
3. What is catalysis? Describe three experiments which illustrate this phenomenon. (Camb. 1st. M.B.)
4. Give an account of three reactions which are usually carried out with the aid of a catalyst. Explain as far as possible the characteristics of catalytic action. (Camb. 1st. M.B.)
5. The products of interaction of two substances often vary with the conditions under which they react. Describe reactions where the nature of the final product is influenced by such factors as temperature, light, or the presence of substances which do not appear to take part in the reaction. (Camb. Schol.)
6. What are the essential features of a catalytic action? Give one example of the uses as catalysts of each of the following: platinum, nickel, aluminium chloride, dilute acid.

CHAPTER X

COLLOIDS

IF a very finely divided solid, such as precipitated chalk, is shaken up with water, a *suspension* of the solid is obtained; that is to say, the particles of solid become distributed throughout the liquid, though they settle out to the bottom in time. The particles of the solid in such a suspension are readily observed by the microscope, and they can be filtered off in the usual way. On the other hand, if a soluble substance such as sugar is shaken with water it dissolves. Although it is known that there are sugar particles in the liquid, they are, of course, quite invisible, they cannot be filtered off, and they do not separate on standing. Thus a distinction can be drawn between *suspensions* of solids in liquids, which contain visible, separable, solid particles on the one hand, and *solutions* on the other, in which the solid particles are so small as to be quite invisible and inseparable, in which, that is to say, the molecular (or ionic) size is comparable with the size of the solvent molecules. In between these two extremes lie those systems known as **colloidal solutions**, in which the size of the particles is intermediate between that of suspensions and true solutions. The existence of colloidal solutions was first realised by Graham (1850) in his experiments on diffusion. He found that whereas solutions of salts would pass easily through parchment or similar membranes, substances such as albumen or glue would not. Substances of the first class he called crystalloids; substances of the second kind colloids, because the colloids with which he was familiar were glue-like substances. The process of separation by a parchment membrane he called **dialysis**, and it is widely used for the purification of colloids. Thus to purify egg-albumen, a typical colloid of the type with which Graham worked, from salt impurities, it is placed inside a parchment bag, or a vessel closed at one end with parchment, while distilled water flows round the outside (Fig. 63). The salts pass through the parchment membrane, while the colloidal albumen remains behind.

Although Graham restricted the term 'colloid' to organic

substances of jelly-like character, it now embraces 'solutions' of quite a different character, and colloidal solutions it is now realised need be neither viscous nor organic. Colloidal solutions have in fact been prepared of a very large number of inorganic substances, including metals, and it even appears probable that almost any substance may under appropriate conditions be brought into the colloidal state. Colloidal solutions are simply solutions in which the particles are greater than a certain size, or, conversely, suspensions in which the particles are less than a certain size. Actually the diameter of the particles in most colloidal solutions lies between

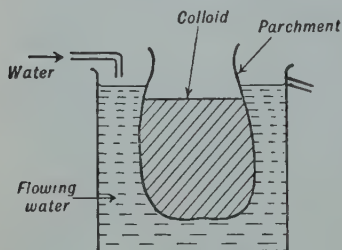


FIG. 63.—DIALYSIS.

10^{-7} and 10^{-5} cms. Von Weimarn, making use of this conception, has shown that by causing precipitation of a substance to be sufficiently rapid, the growth of the particles is prevented and the substance is formed in the colloidal state. Thus if a very concentrated solution of a very soluble barium salt (usually the thiocyanate) is mixed with a very concentrated solution of a

sulphate, barium sulphate is precipitated not in its usual granular form, but as a jelly. Similarly colloidal solutions of other salts, which Graham regarded as typical crystalloids, are obtained by adding their concentrated aqueous solutions to alcohol in which they are insoluble. The salt separates so rapidly that the particles have no time to grow to microscopic size; in other words, it forms a colloidal solution. It is most important to realise this continuous transition from mechanical suspensions on the one hand and true solutions on the other to colloidal solutions, occupying an intermediate position.

The most obvious distinction between colloidal solutions and true solutions is one of particle size, and this may be demonstrated by a phenomenon known as the **Tyndall effect**. If a beam of light is passed through a true solution it is invisible when viewed sideways. Introduction of a colloidal solution, however, causes the light to become visible since the colloid particles scatter the light. The transition between true solution, colloid solution and suspension may be very well seen by shining a beam of light through a solution of sodium thiosulphate to which dilute hydrochloric acid

has been added. The solution is at first clear, but as sulphur is liberated in a colloidal form, the beam of light becomes visible. After some time when the sulphur particles have coagulated and settled out as a precipitate the solution is again clear. The growth in particle size during aggregation may be followed by the colour change, in the scattered light, from blue to red. The Tyndall effect is the basis of the **ultra-microscope** (Fig. 64), a device which renders colloid particles microscopically

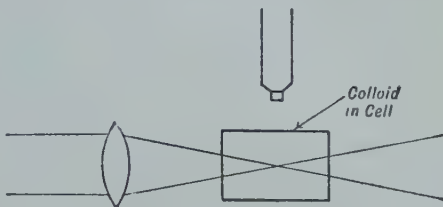


FIG. 64.—ULTRA-MICROSCOPE.

visible as points of light when viewed sideways. Though the particles themselves are too small to be observed, the light which each particle scatters is clearly seen. The formation of a Tyndall effect is one of the principal differences between colloidal and true solutions. Other distinctions depending upon stability, electrical properties, etc., will be discussed later.

Classification of Colloidal Solutions.

The term 'colloid' is a very wide one. It includes smokes, jellies, emulsions, colloidal solutions of metals, oxides, and salts, and other types, and some kind of classification is therefore necessary. The subject is complicated by the various terminologies that have been adopted, and only an outline can be given here. To colloidal solutions in general the name 'sol' is given, though when the solution is so concentrated that it becomes semi-solid the name 'gel' is employed. The medium in which the colloidal solution is formed is the 'dispersion medium'; the substance forming the colloidal solution is called 'the disperse phase.' A preliminary classification is possible thus :

Dispersion Medium.	Disperse phase.	Classification.
Gas	{ Liquid Solid	Fogs Smokes
Liquid	{ Gas Liquid Solid	Foams Emulsions Suspensoid sols and gels.

The most important class is that of suspensoid sols, and various subdivisions of this class exist. The most significant classification is that into *lyophobic* (having no affinity for the solvent) and *lyophilic* (having considerable affinity), and this distinction depends on the *reversibility* of the colloid. A metal, for instance, when once precipitated from its colloidal state—say, in water—will not become colloidal again by the addition of more water. It is *irreversible* or lyophobic. On the other hand, gelatine or starch will, as is well known, easily revert to the colloidal jelly-like state. These are *reversible* or lyophilic colloids, and this is true of most gels. There are other distinctions between lyophobic and lyophilic colloids—for instance, lyophobic, irreversible colloids show a strong Tyndall effect: lyophilic, reversible colloids show only a weak one. Other differences will be mentioned later.

The Preparation of Colloids.

Since colloid particles are intermediate in size between those of true solutions and those of suspensions, two general methods for the preparation of colloidal solutions suggest themselves. A substance may be broken up so that its particle size becomes reduced to that of a colloid in some solvent in which it is insoluble, *i.e.* large particles may be *dispersed*. Secondly, a substance may be precipitated in a suitable medium, *i.e.* small particles such as are present in a true solution may be *aggregated*.

Dispersion Methods.

The most important of dispersion methods is *Bredig's arc method* for the preparation of colloidal metals. An arc is passed between two poles of the metal under the surface of the pure solvent. Presumably the metal is vaporised in the arc, and then so rapidly condensed that it is formed as a colloid. The solvent must be very pure, *e.g.* if water is used it must be conductivity water. In this way colloidal solutions of a very large number of metals have been obtained.

With certain substances vigorous grinding or rubbing beneath the surface of the solvent is sufficient to produce a colloidal solution, *e.g.* gamboge. Similarly if some liquids (*e.g.* nitrobenzene) are very vigorously shaken with water, colloidal solutions (emulsions) are obtained.

Lyophilic colloids (*e.g.* starch) form colloidal solutions as already mentioned merely by heating or shaking with water.

Aggregation or Condensation Methods.

These methods are much more common than dispersion methods, and they simply depend on the principle that when a substance is very rapidly liberated (*e.g.* by a chemical reaction) in a medium in which it is very insoluble, it will tend to form a colloidal solution. Thus *double decomposition* is a widely used method of producing colloidal solutions. As already mentioned, when hydrochloric acid is added to sodium thiosulphate the sulphur set free often forms a colloidal solution. If arsenic sulphide is formed by the action of hydrogen sulphide upon very dilute arsenious oxide solution, it does not usually coagulate, but forms a bright yellow sol. A brown sol of manganese dioxide is often inadvertently prepared by carrying out potassium permanganate titrations in the absence of sulphuric acid. Silica is readily prepared in the colloidal state by the addition of hydrochloric acid to sodium silicate, the silica 'gel' which is deposited on standing being washed free from salt.

Insoluble substances are, of course, frequently set free in the colloidal state by reactions other than double decompositions. *Reduction methods* have been frequently used in the preparation of colloidal metals. Sols of gold, platinum, silver, lead, etc., are quite easily obtained by the reduction of very dilute solutions of the metal salts with some appropriate reducing agent. The reducing agents employed are usually organic, *e.g.* formaldehyde, hydrazine, or a tartrate.

Sols of oxides and hydroxides are usually prepared by *hydrolysis*. The ordinary deep yellow colour of ferric chloride solution is due to the fact that the hydrolysis $\text{FeCl}_3 + 3\text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})_3 + 3\text{HCl}$ produces ferric hydroxide, which remains as a colloidal solution. A pure sol of ferric hydroxide may be obtained by submitting the solution to dialysis. If the hydrolysis is repressed by the addition of hydrochloric acid, the colour becomes much paler. Hydrated oxides readily form colloidal solutions often of the gel type, and the difficulty sometimes experienced in dealing with these substances in qualitative analysis is due to this.

Finally colloidal solutions of many substances may be obtained by rapidly adding a solvent in which they are insoluble to their

concentrated solution in another solvent. For example if a solution of sulphur in alcohol is added to water the sulphur is first liberated in the colloidal state.

Numerous other methods have of course been employed, but in general they all depend upon this principle of rapid liberation in a suitable medium which does not dissolve the substance.

Peptisation.

Freshly prepared precipitates can sometimes be converted into colloidal form (*i.e.* **peptised**) by the addition of an electrolyte (**peptising agent**), often containing a common ion. Thus the addition of ferric chloride to freshly precipitated ferric hydroxide gives a red-brown-coloured colloidal solution of the latter.

The stability of such colloids is presumably due to the adsorption of ions on the surfaces of the colloid particles. Freshly prepared stannic oxide (stannic chloride poured into water) can be peptised by the addition of hydrochloric acid to give a positively charged colloid and by the addition of potassium hydroxide to give the colloid negatively charged.

The Stability and Precipitation of Colloids.

The fundamental point to be realised in studying this question is that colloid particles are electrically charged.

This may be seen if a colloidal solution is introduced into a U-tube and covered at each end with water, an electrode being placed in each limb (Fig. 65). If a potential difference is applied

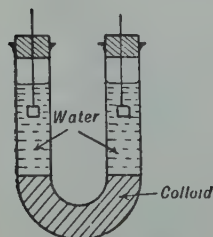


FIG. 65.—CATA-PHORESIS.

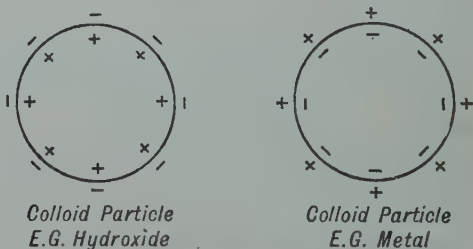


FIG. 66.—HELMHOLTZ DOUBLE LAYER.

across the electrodes, it is found that the colloid moves towards one or other of the electrodes in a similar way to that in which

ions migrate. In the case of the colloid particles, however, their movement is in one direction only. This phenomenon is known as **cataphoresis**, and it shows that colloid particles are charged, all the particles of any one colloid having a similar charge. Different colloids differ in the polarity of their charges. Thus while oxides and hydroxides normally carry positive charges, the particles in colloidal solutions of metals, sulphides, and organic substances like starch are usually negatively charged. The sign of the charge on a particular colloid may sometimes vary with the peptising agent (see above). Since the colloidal solution as a whole is neutral, there must be an equal and opposite charge in the solvent associated with the charges on the colloid particles; in other words, there is associated with each particle an electrical double layer, called the Helmholtz double layer (Fig. 66).

When colloid particles lose their charges they are able to coagulate, and the substance is deposited as a precipitate. Thus if the process of cataphoresis is continued until the particles actually reach the electrode, precipitation occurs as the discharge takes place.

Precipitation by Electrolytes.

It is one of the most important facts of colloid chemistry that addition of an electrolyte to a colloidal solution brings about coagulation and precipitation. The effect is much more marked with lyophobic sols than with lyophilic sols, or gels. The explanation of this precipitation by electrolytes follows from the charged nature of the colloid particles, for the ions of the electrolyte discharge the colloid particles. It would be expected from this that ions with several charges would be more effective precipitants than monovalent ions, and this is in fact the case. Further, in the precipitation of a negatively charged colloid positive ions will be effective. All monovalent positive ions have approximately the same coagulating power; all divalent ions have about one hundred times the coagulating effect of monovalent ions; while trivalent ions are approximately seven times as efficient as divalent ions. These observations are embodied in the **Hardy-Schulze Law**, which states that the coagulating power of an electrolyte depends upon its valency. A familiar example of the principle is in the use of alum to arrest bleeding. Blood is a negative colloid, and the

sols

aluminium ion, with its three positive charges, is therefore a very efficient coagulant. It will be observed that the coagulating power is not in direct proportion to the valency of the ion, and this fact and others suggest that the actual mechanism of colloid precipitation is complicated.

It has already been mentioned that one difference between lyophobic and lyophilic colloids lies in the fact that the latter are not readily precipitated by the addition of electrolytes. So resistant are they that if a lyophilic colloid such as starch is added to a lyophobic colloid it stabilises it against precipitation. This **protective action** of one colloid upon another may be quantitatively expressed in what is termed the 'gold number.' This is the quantity of a protective colloid which must be added to a certain quantity of a gold sol to protect it against coagulation by a standard quantity of sodium chloride. The protective action of some colloids upon others sometimes prevents the easy handling of precipitates in analysis. For this reason in carrying out a complex analysis all organic matter is often removed as a preliminary step.

The characteristic differences between the two classes of colloids are summarised below :

Lyophobic	Lyophilic
(No affinity for solvent)	(Considerable affinity for solvent)
Low viscosity	High viscosity
Normally irreversible (but see peptisation)	Reversible , <i>i.e.</i> will become colloidal again, after coagulation, on addition of solvent
Particles show Tyndall effect, <i>i.e.</i> easily detected by ultra-microscope	Particles not easily detected
Particles are all positively or all negatively charged, <i>i.e.</i> they move in one direction under influence of applied E.M.F.	Particles move in both directions or not at all
Particles coagulate and are precipitated on addition of electrolyte	No precipitation by electrolyte unless added in large quantities, when 'salting out' may occur. Give protection to lyophobic colloids from precipitating effect of electrolytes.
Examples :	Examples :
Metals, sulphur, sulphides	Starch, gum, soaps, <i>i.e.</i> substances of high molecular weight

Applications of Colloid Chemistry.

Knowledge of the properties of colloids has one or two other uses in analytical chemistry. Thus if a precipitate tends to form a colloidal solution an excess of an electrolyte is added and the solution is boiled, as these measures bring about coagulation. In gravimetric analysis the formation of insoluble precipitates is carried out usually at the boiling point and with fairly dilute solutions, as these precautions favour the formation of granular precipitates and diminish adsorption of materials from the solution on the finely divided jelly-like precipitates sometimes obtained.

The study of colloidal solutions has proved important not only in the ways already mentioned, but also in the study of biochemistry. Further, it has yielded valuable information with regard to molecular movement and has enabled a value for the Avogadro number N to be determined. Over 100 years ago the botanist Brown observed that pollen grains suspended in water were in a state of constant random movement. This movement—the ***Brownian movement***, as it is called—has been shown to be characteristic of all minute particles of colloidal size, and may be observed in a large number of colloidal solutions by examination under the ultra-microscope. This perpetual movement is quite independent of outside influences. There is no doubt at all that it is the result of bombardment of the colloid particles by moving molecules: thus the Brownian movement is an ocular demonstration of the kinetic theory. Larger particles such as occur in ordinary suspensions do not move because they are large enough to be struck by a very great number of molecules at any one instant. There is thus a very small probability that this molecular bombardment will communicate a resultant velocity to the particle. With colloid particles, however, which approach more nearly to molecular size it may well be that a given particle will be struck at any particular instant by two molecules, say, moving in one direction and by only one moving in the opposite direction. Hence the colloid particle exhibits the Brownian movement.

The Avogadro Constant. 6.023×10^{23}

Colloidal solutions have been used by Perrin to determine Avogadro's constant, N —that is, the number of molecules in a

gm.-molecule of any substance. Various methods were employed, the one following being the simplest. An emulsion of gamboge in water was prepared, uniformity in the size of the particles being secured by centrifuging. In such an emulsion the particles tend to settle out under gravity, but they are kept in suspension by the pressure exerted by their movement. The fundamental assumption of the method, which must be clearly realised, is that the particles exert a pressure exactly analogous to osmotic pressure by

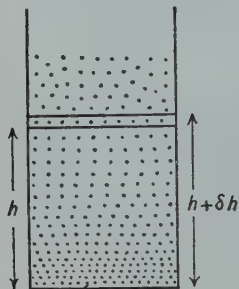


FIG. 67.—PERRIN'S METHOD FOR DETERMINING AVOGADRO'S NUMBER.

reason of their movement under molecular bombardment. It is assumed that the laws applicable to the osmotic pressure of a dissolved substance also apply to the particles of a colloidal solution; *i.e.* the gas laws are assumed to be true for such solutions. The result of the two forces acting upon the particles—gravity on the one hand, and the osmotic pressure on the other—is that the particles distribute themselves throughout the liquid in an equilibrium with a gradually increasing concentration of particles towards the bottom. Let us consider a cylinder of the

gamboge emulsion as shown (Fig. 67), of 1 sq. cm. cross section.

Consider two planes in the cylinder at heights h and $h + \delta h$. If there are n particles per c.c. at a height h , the number of particles contained in the thin slice of liquid between the two planes will be very nearly $n\delta h$. The downward pull on each of these particles due to gravity will be $\varphi(D - d)g$, where φ = the volume of one particle, D = the density of the particles, d = the density of the liquid medium, and g = the acceleration due to gravity.

The downward force due to gravity on *all* the particles in the section is therefore

$$n\delta h\varphi(D - d)g.$$

Let us now apply the kinetic theory of gases (see Chapter III) to these colloid particles. The pressure of a gas is given by $p = \frac{1}{3}mnu^2$ (m = the mass of a molecule, n the number of molecules per c.c., u = their root mean square velocity). If this is assumed to be true for the colloidal solution, the difference in osmotic

pressures due to the particles at heights h and $h + \delta h$ will be given by

$$p - p_1 = \frac{1}{3} m \delta n u^2$$

where δn = number of particles in the thin slice of liquid considered = $n \delta h$.

Now, for 1 gm.-mol. the gas equation is

$$PV = RT,$$

$$\text{or } P = \frac{RT}{V}$$

$$\text{or } \frac{1}{3} n m u^2 = \frac{RT}{V}.$$

Instead of n (the number of molecules per c.c.) we can write $\frac{N}{V}$ (V = the vol. of 1 gm.-mol., N = the number of molecules in 1 gm.-mol.)

$$\therefore \frac{1}{3} \cdot \frac{N}{V} \cdot m u^2 = \frac{RT}{V}$$

$$\text{or } \frac{1}{3} m u^2 = \frac{RT}{N}.$$

Therefore the difference in pressure between the heights h , and $h + \delta h$ is:—

$$p - p_1 = \frac{1}{3} m \delta n u^2 = \frac{RT}{N} \delta n.$$

This is the force which keeps the particles in suspension by balancing the downward pull of gravity.

$$\text{Therefore } \frac{RT}{N} \delta n = n \delta h \phi (D - d) g$$

$$\text{or } \frac{\delta n}{n} = \frac{N}{RT} \cdot \delta h \phi (D - d) g.$$

By integration

$$\log \frac{n_1}{n_2} = \frac{N}{RT} \cdot \phi (D - d) g \cdot h$$

In this equation n_1 and n_2 are the numbers of particles in two different planes, in the suspension, separated by a distance h . These numbers are determined experimentally by counting under the microscope, the instrument being successively focussed on two planes separated by a known distance. The density and

size of the particles may be determined by methods that need not be described here, and hence N may be calculated. The value obtained by this method is 69×10^{22} for the number of molecules in a gm.-molecule.

QUESTIONS ON CHAPTER X.

1. Write a brief account of the preparation and properties of colloidal solutions. In what respects do the physical properties of a colloidal solution of silicic acid differ from those of an aqueous solution of sodium chloride? (N.U.J.B., H.C.)

2. Compare and contrast the following processes: gaseous diffusion, osmotic flow, dialysis. Describe a typical experiment to illustrate each process. (Camb. 1st. M.B.)

3. Describe experiments you have seen for the preparation of colloidal solutions. How would you distinguish a colloidal from an ordinary solution? What is the nature of a colloidal solution and how is it verified? (Camb. 1st. M.B.)

4. What is understood by a colloidal solution? How would you prepare such a solution of silicic acid and ferric hydroxide? What are the properties of colloids? (Camb. 1st. M.B.)

5. How would you prepare colloidal solutions of (a) arsenic trisulphide, (b) platinum? What are the distinctive properties of colloidal solutions? (Camb. 1st. M.B.)

6. What is a colloidal solution? Distinguish between colloidal solution and true solution.

Describe how colloidal solution of (a) any metal, (b) silica may be prepared, and give a brief account of the properties of these solutions. (C.W.B., H.C.)

MISCELLANEOUS QUESTIONS.

1. Explain the following terms: isomorphism, molecular heat, solubility product, electrochemical equivalent. (Camb. Schol.)

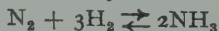
2. Summarise the evidence for one of the following statements:

(a) Avogadro's number is 6×10^{23} .

(b) Mercury vapour behaves as a monatomic gas.

(c) The transport numbers for Ag^+ and NO_3^- in silver nitrate solution are 0.47 and 0.53. (Oxf. Schol.)

3. Ammonia is now made commercially by the exothermic reaction between its elements, represented by



Point out the conditions required for a good yield, and say what you know of the practical application of the principles you have quoted. (Oxf. Schol.)

4. Describe the phenomena which are observed when :

(a) a cane-sugar solution is separated from pure water by a copper ferrocyanide membrane;

(b) a colloidal solution is separated from pure water by a thin animal membrane.

In what way are the phenomena you describe of importance? (Oxf. Schol.)

5. A newly discovered substance is considered to be an element of the seventh group of the periodic classification. What experiments should be carried out (a) to determine its atomic weight, and (b) to justify the assumption that the substance is a member of the halogen sub-group? (Camb. Schol.)

6. How would you endeavour to measure experimentally two of the following quantities :

(a) the equivalent conductivity of acetic acid at infinite dilution ;

(b) the degree of dissociation of iodine vapour at 250°C ;

(c) the heat evolved in the reaction $2\text{Zn} + \text{O}_2 = 2\text{ZnO}$?

(Oxf. Schol.)

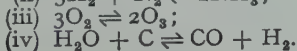
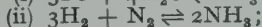
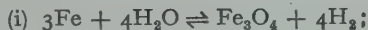
7. How far is the process of solution to be regarded as a simple intermingling of molecules? Illustrate your answer by reference to solutions of (a) NaCl in water, (b) N_2 in water, (c) sulphur in CS_2 , (d) NH_3 in water? (Oxf. Schol.)

8. Determinations of the vapour density of ammonium chloride and of the freezing points of its aqueous solutions indicate that this compound is dissociated both in the vapour and in its solution. What experimental evidence can you give to support the view that the dissociation in the vapour is of a different type from that in the solution? (Camb. Schol.)

9. Define the terms : molecular conductivity, molecular volume, vapour density, heat of reaction.

Indicate briefly the use of these quantities in Chemistry. (Camb. Schol.)

10. Explain the terms 'reversible reaction' and 'chemical equilibrium.' Discuss the effects on these phenomena of (a) change of temperature, (b) change of pressure, (c) relative concentrations of reactants, (d) solid catalysts. Choose your illustrations from the following systems :



(N.U.J.B., H.C.)

11. Describe in outline the various kinds of experimental results which lead us to believe that atoms and molecules have real existence. (N.U.J.B., H.C.)

12. Explain, with two examples of each, what you understand by

the following terms: (a) allotropy, (b) isomorphism, (c) hydrolysis, (d) colloidal solution, (e) critical point. (Lond. H.C.)

13. Outline the experiments and arguments which have led to the adoption of the formula H_2O for water vapour. Describe one of the experiments in detail. (Assume nothing but Avogadro's Rule.)

Explain briefly why the combining volumes of hydrogen and oxygen are not in the exact ratio of 2 : 1. (Oxf. H.C.)

14. State and explain on the basis of fundamental physico-chemical principles the conditions under which the following processes are carried out on the industrial scale:

- (a) the synthesis of ammonia from nitrogen and hydrogen,
 - (b) the manufacture of sulphuric acid by the contact process.
- (C.W.B., H.C.)

15. Discuss three of the following:

- (a) The use of isotonic solutions.
- (b) When a direct electric current is passed between two platinum electrodes immersed in a dilute aqueous solution of sulphuric acid, the quantity of acid present is unchanged.
- (c) When the terminals of an electric battery are applied to a piece of blue litmus paper which has been damped by a solution of sodium chloride a red spot appears.
- (d) When hydrochloric acid is passed into a saturated solution of common salt, the salt is precipitated. (Camb. 1st. M.B.)

16. Discuss concisely the following facts:

- (a) The transport numbers of Ag^+ and NO_3^- in $\frac{N}{10}$ solution at $25^\circ C.$ are 0.477 and 0.523 respectively.
- (b) When sodium chloride solution is added to a colloidal solution of gold a series of colour changes occurs before yellow particles become visible.
- (c) $[Cu(CN)_4]^{--}$ is a complex ion from which no appreciable amount of copper can be precipitated as sulphide by hydrogen sulphide. (O. & C., H.C.)

17. Discuss the part which the study of gases has played in the development of chemical theory. (Oxf. Schol.)

18. Explain three of the following:

- (a) silver cyanide is soluble in excess of potassium cyanide,
- (b) methyl orange can be used as an indicator in titrating sodium carbonate with acids,
- (c) a solution of bismuth chloride gives a precipitate on dilution,
- (d) hydrochloric acid fumes in moist air. (Oxf. Schol.)

19. The following data refer to elements of the halogen series:

Element	F.	Cl.	Br.
Atomic weight	19.0	35.46	79.92
Atomic number	9	17	35

What can be deduced from these numbers as to the nature of the nuclei, the arrangement of electrons, and the valencies of the atoms concerned? (C.W.B., H.C.)

20. Discuss the effect of (a) temperature, (b) pressure, and (c) the proportion of the reacting gases, on the exothermic reaction



and point out the best practical conditions for the industrial production of sulphur trioxide.

Indicate briefly how the process is carried out commercially.

(C.W.B., H.C.)

21. Explain the difference between electrolytic conduction and cataphoresis, and describe how you would demonstrate this difference experimentally. (O. & C. 'S'.)

22. Explain : (a) ionisation constant of an acid; (b) ionic product for water; (c) solubility product; (d) pH.

(i) Calculate the pH of a dilute solution containing equimolecular concentrations of acetic acid and sodium acetate at 20° C. (ionisation constant of acetic acid = 1.9×10^{-5} at 20° C.).

(ii) Calculate the solubility of silver chloride (in moles per litre) in *N*/10-silver nitrate at 20° C. (solubility product of silver chloride = 10^{-10} at 20° C.). (O. & C. 'S'.)

23. What is meant by : (a) monotropy; (b) enantiotropy? Illustrate your answer by reference to the allotropy of phosphorus and tin. (O. & C. 'S'.)

24. What factors can affect the rate at which substances react? Illustrate your answer by examples. What explanation, if any, of the observed effects can you give in terms of the molecular kinetic theory? (O. & C. 'A'.)

25. Explain with the aid of a diagram how the addition of a non-volatile solute affects the vapour pressure, and hence the boiling point and freezing point of a solvent.

What conclusions could be drawn from the following observations : (a) 0.608 gm. of a substance, of empirical formula weight 152, dissolved in 40 gm. of benzene, gave a depression of the freezing point of 0.5° C.; (b) 0.70 gm. of a substance of empirical formula weight 58.5, dissolved 100 gms. of water, gave a depression of 0.4° C.?

(Depression constants for 100 gms. of : (a) benzene, 49.95° C.; (b) water, 18.6° C.). (O. & C. 'A'.)

26. Illustrate by reference to the Periodic Table what you understand by the terms : short period; inert gas; sub-group; transition element; valency electron. (O. & C. 'A'.)

27. Define osmosis, osmotic pressure of a solution.

Show how the osmotic pressure of a solution is related to the lowering of the vapour pressure of the solvent. (O. & C. 'A'.)

28. What do you understand by : (a) the heat of formation of a metallic oxide, and (b) the electrode potential of a metal?

Show how these quantities are related to the chemical character of the metals concerned. Illustrate your answer by particular reference to sodium, zinc and lead. (O. & C. 'A'.)

29. The heat of combustion of ethyl alcohol is $-341,800$ calories, and the heat of formation of carbon dioxide and water are $-96,000$ and $-68,000$ calories respectively, all measurements referring to similar conditions. What is the heat of formation of ethyl alcohol under these conditions?

The heat of formation of the C—C link (as in ethane) is $81,600$ calories, that of the C=C link (as in ethylene) is $146,100$ calories, and that of the C≡C link (as in acetylene) is $192,100$ calories. How would you expect the reactivity of the three hydrocarbons to differ in the light of these data? (O. & C. 'S'.)

30. Explain concisely the difference between three of the following : (a) a weak and a strong electrolyte; (b) electrovalency and covalency; (c) cooling by adiabatic expansion and the Joule-Thomson effect; (d) dissociation and thermal decomposition; (e) monotropy and enantiotropy. (O. & C. 'S'.)

31. Calculate the approximate pH values of the solutions obtained by adding 20, 24, 24.9 and 25 c.c. of decinormal sodium hydroxide to 25 c.c. of decinormal hydrochloric acid.

Why would the values be different if decinormal acetic acid were used instead of hydrochloric, and what would be the effect in each case if ammonium hydroxide were substituted for sodium hydroxide?

(O. & C. 'S'.)

32. Write down the expression for the equilibrium constant of the reaction



(a) If a is the fraction of ammonia present by volume in an equilibrium mixture made from one volume of nitrogen and three volumes of hydrogen, and P is the total pressure, show that

$$a/(1-a)^2 = kP,$$

where k is a constant.

[It will be found convenient to express concentrations as partial pressures.]

If 0.25 of the equilibrium mixture at 400°C. and 100 atmospheres pressure is ammonia, calculate what fraction of the mixture will be ammonia at 10 atmospheres, at that temperature.

(b) The equilibrium constant varies with temperature according to the equation

$$\log K_1 - \log K_2 = \frac{13,200}{2.303} \left(\frac{1}{T_1} - \frac{1}{T_2} \right),$$

where K_1 and K_2 are the constants at T_1 and T_2 respectively.

In the light of this equation and your results in (a) explain very briefly the conditions used in the manufacture of ammonia. Why is it necessary to use a catalyst? (O. & C. 'S'.)

33. Why is a distinction made between weak and strong electrolytes? Illustrate by practical examples how the characteristics of weak electrolytes can be made use of in qualitative analysis.

(O. & C. 'S'.)

34. A solution of a salt containing potassium and iron was electrolysed in series with a silver voltameter. At the conclusion of the experiment 0.563 gm. of silver was deposited in the voltameter, and a measured volume of the anode liquid contained 0.601 gm. of iron and 1.459 gm. of potassium. In the original salt this weight of potassium was combined with 0.528 gm. of iron. What conclusions do you draw from the experiment, and what is the valency of the complex ion containing one atom of iron?

$$(\text{Fe} = 56, \text{Ag} = 108)$$

(O. & C. 'S'.)

35. Discuss the valency of nitrogen in the four compounds: ammonia; ammonium chloride; ethyl nitrite; nitro-benzene.

(O. & C. : H.C.)

36. Hydrogen chloride gas is allowed to dissolve in a normal solution of sodium acetate. Plot graphs to show qualitatively the change in pH and the change in conductivity as hydrogen chloride is added. (You are recommended to make rough calculations of the pH of the solution when the following amounts of hydrogen chloride have dissolved :

0, 0.1, 0.5, 0.9, 1.0, 1.1, 2.0 moles per litre.

Dissociation constant of acetic acid = 2×10^{-5} moles/litre.

Ionic product of water = 10^{-14} (moles/litre)².

Ratio of ionic mobilities = $\text{H}^+ : \text{Cl}^- : \text{Ac}^- :: 10 : 2 : 1.$

(Camb. Schol.)

37. Suggest simple experiments to test the following statements :

- Benzoic acid dissolved in benzene forms double molecules.
- Unlike most salts, mercuric chloride is a weak electrolyte in aqueous solution.
- When AgCN is dissolved in excess of KCN solution a complex ion of formula $\text{Ag}(\text{CN})_2^-$ is formed.
- Copper and nickel form a continuous range of solid solutions at high temperatures.

(Camb. Schol.)

38. State Raoult's Law.

The vapour pressure of a certain pure liquid at 20° C. is 120 mm. Hg. An equimolecular mixture of the liquid with another at the same temperature is found to exert a pressure of one atmosphere. Assuming the solution to obey Raoult's Law, obtain the vapour pressure of the second component. (Camb. Schol.)

39. Discuss the influence of pressure on chemical equilibria in the gaseous state.

x gm. mols. of nitrogen are sealed in a vessel at constant volume with $3x$ gm. mols. of hydrogen, and the system is brought to equilibrium.

Deduce an expression for the equilibrium constant governing the formation of gaseous ammonia in terms of x , the total pressure P and the fraction, a , of nitrogen molecules which have been converted. Show that when a is small, it is directly proportional to P .

40. What does the term pH of a solution mean, and how may it be measured?

A solution containing 12.95 gm. of aniline hydrochloride in 100 ml. of 0.01*N*-hydrochloric acid is brought into equilibrium with 100 ml. of benzene. If the amount of aniline in the benzene is found to be 0.1 gm., what is the hydrolysis constant of aniline hydrochloride?

(The partition coefficient for aniline between benzene and water is given by $C_b/C_w = 10$.) (Camb. Schol.)

41. A mixture of two completely miscible liquids sometimes gives rise on solidification to a compound of the two constituents, and sometimes to a eutectic mixture. Give examples of each case, and describe tests that can be applied to establish the fact of compound formation and to show that eutectic mixtures are not compounds.

(Camb. Schol.)

42. What is meant by the phrase the electrochemical series of metals?

What experiments could be made to place copper, nickel and tin in their correct order in this series? (Oxf. Schol.)

43. Discuss the valency of phosphorus in the compounds of formulæ PH_3 , PH_4I , PCl_3 , PCl_5 , POCl_3 , H_3PO_2 , H_3PO_3 , H_3PO_4 .

(Oxf. Schol.)

44. Draw the pressure-concentration (constant-temperature) diagrams to illustrate the various types of vapour-pressure curve given by systems of two volatile liquids, the liquids being miscible in all proportions.

In one case draw the corresponding temperature-concentration (constant-pressure) diagram, and discuss what will happen when a representative mixture of the two liquids is fractionally distilled.

(Camb. Schol.)

45. Show that the pH of a partially neutralised solution of a weak acid is given by

$$\text{pH} = \text{pK} - \log (\text{conc. acid}/\text{conc. salt}),$$

where $\text{pK} = -\log Ka$, Ka being the dissociation constant of the acid (you may assume that the salt of the acid is completely ionised).

If you were given decinormal solutions of two similar weak acids, a decinormal solution of sodium hydroxide and a suitable indicator, how would you determine the dissociation constant of one of the acids if that of the other was already known? (Camb. Schol.)

46. Discuss briefly the applications of the Law of Mass Action to electrolytic equilibria. How would you expect the solubility of a moderately soluble salt to be affected by the addition of an electrolyte not containing a common ion? (Camb. Schol.)

47. Write notes on the following eutectic, azeotropic mixture, triple point, degree of freedom, solid solution. (Oxf. Schol.)

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For further reading the following may be recommended, and might well find a place in all science libraries. The list is not, of course, intended to be in any way exhaustive.

General.

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Glasstone : *Recent Advances in Physical Chemistry*.

W. C. McC. Lewis : *A System of Physical Chemistry*. (Vol. I.)

Books on Special Subjects.

Freund : *The Study of Chemical Composition*.

(Very full accounts of classical work : to be consulted in connection with Chap. I.)

Sidgwick : *The Electronic Theory of Valency*. (For Chap. II.)

Hinshelwood : *The Kinetics of Chemical Change in Gaseous Systems*. (Chaps. VI and IX.)

Hinshelwood : *Thermodynamics for Students of Chemistry*.

Findlay : *The Phase Rule*. (Chap. IV.)

Sir W. H. Bragg and W. L. Bragg : *X-Rays and Crystal Structure*. (Chap. III.)

Aston : *Isotopes*. (Chap. II.)

Rideal and Taylor : *Catalysis in Theory and Practice*. (Chap. IX.)

Two reprints of lectures delivered to the Science Masters Association may prove useful. They are *The Ionic Theory of Electrolytic Dissociation* (Sir Harold Hartley), and *Atomic Structure and the Periodic Table* (Sidgwick).

Practical Physical Chemistry.

Findlay : *Practical Physical Chemistry*.

Sherwood Taylor : *Elementary Practical Physical Chemistry*.

Philbrick : *Problems in Practical Physical Chemistry*.

ANSWERS TO NUMERICAL QUESTIONS

CHAPTER I.

- | | |
|--|--|
| <p>10. (a) 26.94; (b) 20.16.
 11. 121.8; X_4O_6, $(XO_2)_n$, $(X_2O_3)_n$.
 13. 133.
 14. 24.4.
 15. Probable Atomic Weight 56.
 Equivalents 28.0, 18.66.
 17. <i>M</i> At. Wt. 209.0, trivalent.
 <i>G</i> At. Wt. 130, monatomic.
 18. 9.08.
 19. 127; X_2O_5.
 20. Li 6.9, Ag 107.9, Cl 35.5.
 23. At. Wt. 200.6; Mol. Wt. of
 vapour 199.4; Ratio of speci-
 fic heats 1.66.</p> | <p>24. 9.1.
 25. C_8O_2.
 26. 15 c.c. H_2, 5 c.c. CH_4, 5 c.c. CO_2.
 28. Mixture 1 part H_2, 1 part CH_4;
 or 3 parts H_2, 1 part C_2H_6; or
 5 parts H_2, 1 part C_4H_{10}, etc.;
 41.25.
 29. 118.6.
 30. 227.3.
 31. 89.3% dissociated into NO_2.
 32. 20.1% dissociated.
 34. 81.0% dissociated.
 35. Vapour density of iodine 83.15;
 52.73% dissociated.</p> |
|--|--|

CHAPTER III.

2. 0.082 litre atmos. per $^{\circ}C$.; 2 cal. per $^{\circ}C$.; 40,970 cm. per sec.

CHAPTER IV.

- | | |
|---|--|
| <p>8. 80.5% $C_2H_4Br_2$; 19.5% H_2O.
 9. 122
 10. 49.6 mm.
 11. 28 : 100.
 15. 2.4 gm.</p> | <p>16. 9; (a) 0.09<i>N</i>, (b) 0.0818<i>N</i>.
 24. 35.6% O_2, 64.4% N_2.
 25. 71 c.c.; 10.6% N_2, 19.0% O_2,
 70.4% CO_2.
 26. (a) $\frac{5}{8}$ atmos.; (b) $\frac{3}{8}$ atmos.</p> |
|---|--|

CHAPTER V.

- | | |
|--|---|
| <p>1. 6.91 atmos.
 2. 982.6 cm.
 3. 182.
 4. 178.3.
 5. 1.29 gm. per litre.
 8. 0.0812 litre atmos.
 10. 86%.
 11. 25.52 atmos.
 12. 50%.
 14. 193.
 15. 107.
 16. 92.5.
 17. 92.2; 17.2 atmos.
 18. 72%.
 19. 17.44 mm.
 20. 236.</p> | <p>21. 167.7.
 22. 92.
 23. 2.
 25. 76.7%.
 27. 324.
 28. 57.
 29. 192.
 30. 70° C. per 100 gm.
 31. 342.
 33. 160; 265.5.
 36. - 3.03° C.
 37. 77%.
 38. 7.3×10^{-3} gm. ion per litre.
 41. 69.8° C. per 100 gm.
 42. 43 cal. per gm.
 43. 129.4 cal. per gm.</p> |
|--|---|

CHAPTER VI.

2. 144.6 mins.
4. 0.53; 13.73 mins.
5. 82.4 mins.
7. 3.2 (concentrations in gm. equiv. per litre, time in minutes).
9. (a) 0.9 mols.; (b) 0.54 mols.
10. 1.16% by volume.
12. 5.58 mols. HI, 2.21 mols. H₂, 0.21 mols. I₂.
13. 2.21 mols. H₂, 2.21 mols. I₂.
16. 5.28 atmos.
17. 0.048 equivalents Br.
20. 143.7 mm.; 34.8 mm., 725.2 mm.
24. 33; 0.28 dissociated.

CHAPTER VII.

1. — 99,000 cal.
2. — 50,000 cal.
3. 28.8 Cals.
4. (a) — 29,000 cal.; (b) — 29,290 cal.
5. — 33,900 cal. constant volume; — 36,192 cal. constant pressure.
7. — 110,000 cal.
8. 31,310 cal. evolved.
9. — 160,925 cal.
10. — 227, 600 cal.
13. — 129,400 cal.

CHAPTER VIII.

1. 0.00033 gm.
2. 0.27 amp.
3. 3.43 gm., 3.30 gm.
4. 0.357 gm.; 40 c.c.
8. Ag 0.46, NO₃ 0.54.
9. Cu 0.42, SO₄ 0.58.
10. Cl 0.17, H 0.83.
11. Cu 0.216 } assuming unit volume
SO₄ 0.784 } represents complete anode compartment.
13. 93%
14. 0.00277 rec. ohm.; 138.5 rec. ohms.
15. 0.145 gm.-ion per litre.
16. 43.2, 62.1; 0.000448 cm. per sec.; 0.000644 cm. per sec.
18. 4.52%, 0.000452 per litre.
19. 346.9.
22. 1.52%.
23. 1.33×10^{-3} gm.-ion per litre.
24. 10^{-4} gm.-ion per litre.
25. 1.99×10^{-5} ; 4.43×10^{-4} gm.-ion per litre.
26. 4.5%; 0.48N.
27. From 0.0014 to 2.14×10^{-5} gm.-ion per litre.
29. 1.09×10^{-10} .
30. 0.0011 gm. per litre.
31. 1×10^{-10} ; 2.33×10^{-7} gm. per litre.
35. 0.0014 gm.
36. (a) 1.15%; (b) 0.00227%.
37. 6.46×10^{-5} gm. per litre.
44. 3.45 : 1.
46. 2 : 1 approx.
47. 3.1 : 1.
49. (a) 0.77×10^{-5} ; (b) 0.87%.
51. 0.93×10^{-5} gm.-ion per litre.
52. 10^{-7} approx.
54. 180 c.c. approx.

MISCELLANEOUS QUESTIONS.

22. (i) 4.28; (ii) 10^{-9} .
29. — 54,200 cal.
32. (a) 0.04%.
34. 4.
38. 1400 mm.
40. 1.4×10^{-4} .

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ATOMIC WEIGHTS

Element.	Symbol.	Atomic Number.	Accurate Atomic Weight.	Approximate Atomic Weight.
Aluminium .	Al	13	26.97	27
Antimony .	Sb	51	121.76	122
Argon .	A	18	39.944	40
Arsenic .	As	33	74.91	75
Barium .	Ba	56	137.36	137
Beryllium .	Be	4	9.02	9
Bismuth .	Bi	83	209.0	209
Boron .	B	5	10.82	11
Bromine .	Br	35	79.916	80
Cadmium .	Cd	48	112.4	112
Calcium .	Ca	20	40.08	40
Carbon .	C	6	12.00	12
Chlorine .	Cl	17	35.457	35.5
Chromium .	Cr	24	52.01	52
Cobalt .	Co	27	58.94	59
Copper .	Cu	29	63.57	63.6
Fluorine .	F	9	19.00	19
Gold .	Au	79	197.2	197
Helium .	He	2	4.002	4
Hydrogen .	H	1	1.0078	1
Iodine .	I	53	126.92	127
Iron .	Fe	26	55.84	56
Krypton .	Kr	36	83.7	84
Lead .	Pb	82	207.22	207
Lithium .	Li	3	6.94	7
Magnesium .	Mg	12	24.32	24
Manganese .	Mn	25	54.93	55
Mercury .	Hg	80	200.61	200
Neon .	Ne	10	20.183	20
Nickel .	Ni	28	58.69	59
Nitrogen .	N	7	14.008	14
Oxygen .	O	8	16.000	16
Phosphorus .	P	15	31.02	31
Platinum .	Pt	78	195.23	195
Potassium .	K	19	39.096	39
Selenium .	Se	34	78.96	79
Silicon .	Si	14	28.06	28
Silver .	Ag	47	107.88	108
Sodium .	Na	11	22.997	23
Strontium .	Sr	38	87.63	88
Sulphur .	S	16	32.06	32
Tellurium .	Te	52	127.61	128
Tin .	Sn	50	118.7	118
Vanadium .	V	23	50.95	51
Xenon .	Xe	54	131.3	131
Zinc .	Zn	30	65.38	65

N.B.—The approximate atomic weights to be used in calculations.

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	9	13	17	21	26	30	34	38
											4	8	12	16	20	24	28	32	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	12	15	19	23	27	31	35
											4	7	11	15	19	22	26	30	33
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	11	14	18	21	25	28	32
											3	7	10	14	17	20	24	27	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	7	10	13	16	20	23	26	30
											3	7	10	12	16	19	22	25	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	28
											3	6	9	12	15	17	20	23	26
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	9	11	14	17	20	23	26
											3	5	8	11	14	16	19	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	14	16	19	22	24
											3	5	8	10	13	15	18	21	23
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	3	5	8	10	13	15	18	20	23
											2	5	7	10	12	15	17	19	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
											2	5	7	9	11	14	16	18	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
											2	4	6	8	11	13	15	17	19
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8

LOGARITHMS

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	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7529	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	3	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6-7	8	9
-00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2
-01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2
-02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2
-03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	2	2
-04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	1	2	2
-05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	1	2	2
-06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	1	2	2
-07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	1	2	2
-08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	1	2	2
-09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	1	2	2
-10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	1	2	2
-11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	1	2	2	2
-12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	1	2	2	2
-13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	1	2	2	2
-14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	1	2	2	2
-15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	1	2	2	2
-16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	1	2	2	2
-17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	1	2	2	2
-18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	1	2	2	2
-19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	1	2	2	2
-20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	1	2	2	2
-21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	1	2	2	2	2
-22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	1	2	2	2	2
-23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	1	2	2	2	2
-24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	1	2	2	2	2
-25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	1	2	2	2	2
-26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	1	2	2	2	2
-27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	1	2	2	2	2
-28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	1	2	2	2	2
-29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	1	2	2	2	2
-30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	1	2	2	2	2
-31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	1	2	2	2	2
-32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	1	2	2	2	2
-33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	1	2	2	2	2
-34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	1	1	2	3	3	3
-35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	1	1	2	3	3	3
-36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	1	1	2	3	3	3
-37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1	1	1	1	2	3	3	3
-38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	1	1	2	3	3	3
-39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	1	1	2	3	3	3
-40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	1	1	2	3	3	3
-41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	1	1	2	3	3	3
-42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	1	1	2	3	3	3
-43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	1	1	2	3	3	3
-44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2814	1	1	1	1	2	3	3	3
-45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	1	1	2	3	3	3
-46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	1	1	2	3	3	3
-47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	1	1	2	3	3	3
-48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	1	1	2	3	3	3
-49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	1	1	2	3	3	3

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	6	9
-50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7
-51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7
-52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
-53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
-54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
-55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
-56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
-57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
-58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8
-59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
-60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	9
-61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
-62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9
-63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
-64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
-65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
-66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10
-67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
-68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
-69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10
-70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	11
-71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
-72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11
-73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
-74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
-75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
-76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
-77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
-78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
-79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13
-80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
-81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
-82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
-83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
-84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
-85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
-86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
-87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
-88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
-89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
-90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
-91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
-92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
-93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
-94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
-95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
-96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19
-97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
-98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
-99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	20



THE ARRANGEMENT OF ELECTRONS IN THE

Transition
elements (

Transition
elements (

	1s	2s 2p	3s 3p 3d	4s 4p 4d 4f	5s 5p 5d	6s 6p 6d	7s
1 H	1						
2 He	2						
3 Li	2	1					
4 Be	2	2					
5 B	2	2 1					
6 C	2	2 2					
7 N	2	2 3					
8 O	2	2 4					
9 F	2	2 5					
10 Ne	2	2 6					
11 Na	2	8	1				
12 Mg	2	8	2				
13 Al	2	8	2 1				
14 Si	2	8	2 2				
15 P	2	8	2 3				
16 S	2	8	2 4				
17 Cl	2	8	2 5				
18 A	2	8	2 6				
19 K	2	8	8	1			
20 Ca	2	8	8	2			
21 Sc	2	8	8 1	2			
22 Ti	2	8	8 2	2			
23 V	2	8	8 3	2			
24 Cr	2	8	8 5	1			
25 Mn	2	8	8 5	2			
26 Fe	2	8	8 6	2			
27 Co	2	8	8 7	2			
28 Ni	2	8	8 8	2			
29 Cu	2	8	8 10	1			
30 Zn	2	8	8 10	2			
31 Ga	2	8	18	2 1			
32 Ge	2	8	18	2 2			
33 As	2	8	18	2 3			
34 Se	2	8	18	2 4			
35 Br	2	8	18	2 5			
36 Kr	2	8	18	2 6			
37 Rb	2	8	18	8	1		
38 Sr	2	8	18	8	2		
39 Y	2	8	18	8	2		
40 Zr	2	8	18	8 1	2		
41 Nb	2	8	18	8 4	2		
42 Mo	2	8	18	8 5	1		
43 Tc	2	8	18	8 6	1		
44 Ru	2	8	18	8 7	1		
45 Rh	2	8	18	8 8	1		
46 Pd	2	8	18	8 10			

ATOMS OF THE ELEMENTS IN THEIR NORMAL STATES

	1s	2s 2p	3s 3p 3d	4s 4p 4d 4f	5s 5p 5d	6s 6p 6d	7s
47 Ag	2	8	18	8 10	1		
48 Cd	2	8	18	8 10	2		
49 In	2	8	18	18	2 1		
50 Sn	2	8	18	18	2 2		
51 Sb	2	8	18	18	2 3		
52 Te	2	8	18	18	2 4		
53 I	2	8	18	18	2 5		
54 Xe	2	8	18	18	2 6		
55 Cs	2	8	18	18	8	1	
56 Ba	2	8	18	18	8	2	
57 La	2	8	18	18	8 1	2	
58 Ce	2	8	18	18 1	8 1	2	
59 Pr	2	8	18	18 2	8 1	2	
60 Nd	2	8	18	18 3	8 1	2	
61 Pm	2	8	18	18 4	8 1	2	
62 Sm	2	8	18	18 5	8 1	2	
63 Eu	2	8	18	18 6	8 1	2	
64 Gd	2	8	18	18 7	8 1	2	
65 Tb	2	8	18	18 8	8 1	2	
66 Dy	2	8	18	18 9	8 1	2	
67 Ho	2	8	18	18 10	8 1	2	
68 Er	2	8	18	18 11	8 1	2	
69 Tm	2	8	18	18 12	8 1	2	
70 Yb	2	8	18	18 13	8 1	2	
71 Lu	2	8	18	18 14	8 1	2	
72 Hf	2	8	18	32	8 2	2	
73 Ta	2	8	18	32	8 3	2	
74 W	2	8	18	32	8 4	2	
75 Re	2	8	18	32	8 5	2	
76 Os	2	8	18	32	8 6	2	
77 Ir	2	8	18	32	8 7	2	
78 Pt	2	8	18	32	8 8	2	
79 Au	2	8	18	32	8 10	1	
80 Hg	2	8	18	32	8 10	2	
81 Tl	2	8	18	32	18	2 1	
82 Pb	2	8	18	32	18	2 2	
83 Bi	2	8	18	32	18	2 3	
84 Po	2	8	18	32	18	2 4	
85 At	2	8	18	32	18	2 5	
86 Rn	2	8	18	32	18	2 6	
87 Fr	2	8	18	32	18	8	1
88 Ra	2	8	18	32	18	8	2
89 Ac	2	8	18	32	18	8 (1)	2
90 Th	2	8	18	32	18	8 (2)	2
91 Pa	2	8	18	32	18	8 (3)	2
92 U	2	8	18	32	18	8 (4)	(2)

Transition elements — The rare earths

Transition elements —

